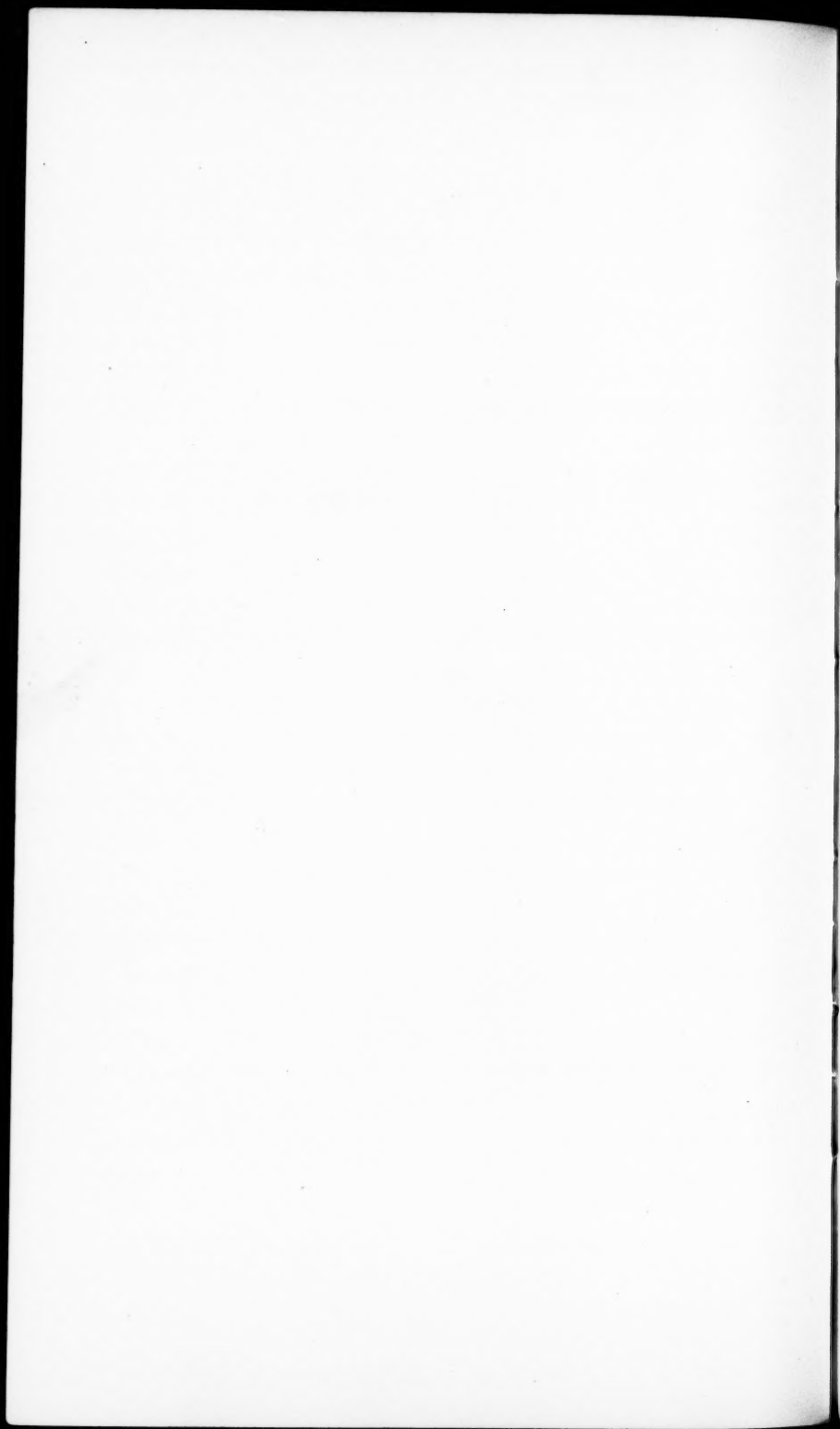


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CERTAIN PHYSICAL PROPERTIES OF SINGLE CRYSTALS
OF TUNGSTEN, ANTIMONY, BISMUTH, TELLURIUM,
CADMIUM, ZINC, AND TIN.

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INTRODUCTION.

THE importance of a knowledge of the physical properties of single crystals of the metals requires no argument. Very little is known of the subject, however. Until within a few years, practically all that we had was a determination of the three elastic constants of a natural

crystal of copper, and of its electrical resistance and thermal conductivity at low temperatures, and questionable data on the thermal expansion and electrical properties of bismuth. Recently the metallurgists have studied the properties of single crystals particularly with regard to plastic flow when stressed beyond the elastic limit, in order to better understand the behavior of crystalline aggregates when stressed beyond the elastic limit, and we now have a rather complete knowledge of the phenomena of flow in single crystals of aluminum, zinc, and tin.¹ Within a year, and after a good part of this present investigation was completed, Grüneisen and Goens² have published data for the elastic constants, thermal expansion, and electrical resistance of single crystals of zinc and cadmium. With the exception of the single crystal of copper, this seems to be the first knowledge of the detailed elastic constants of any metal, as distinguished from the average constants given by an isotropic aggregate. Several years previously I had found very great differences of the linear compressibility of a number of metals in different directions, but had not sufficient data for the detailed constants.³

The need of a detailed study of the properties of single crystals is greatest in those metals which do not crystallize in the cubic system, because many of the properties of a cubic crystal are the same in all directions, and therefore will be the same for a single crystal as for an isotropic aggregate, of which we already have sufficient knowledge. Among such properties are the linear compressibility, thermal expansion, electrical resistance, and thermal conductivity. Three elastic constants are required for the crystal, however, against two for the aggregate.

In this paper I have studied particularly the more readily obtainable non-cubic metals, namely antimony, bismuth, and tellurium, (trigonal), cadmium and zinc, (hexagonal), and tin (tetragonal). Also, because I was fortunate enough to obtain a fine single crystal of tungsten, I have determined certain of its properties. The properties of these metals which I have examined are as follows. (1) Thermal Expansion. In all of the cases above, except tungsten, two constants are sufficient to determine the thermal expansion. These are the constants which give the expansion along an axis of three-, four-, or six-fold symmetry, and the expansion in every direction at right angles to such an axis. They may most easily be determined by measuring the linear expansion of rods cut along one or the other of these directions. The expansion determined in the following is for a small range of temperature on both sides of room temperature.

(2) Electrical Resistance. The symmetry relations of electrical resistance are like those of thermal expansion, and the requisite constants may also be determined by measurements on samples lying along the axis or at right angles to it. I have determined the specific resistance for the necessary directions, the temperature coefficient of resistance between 0° and 100° C. as a function of direction, and the effect of hydrostatic pressures up to 12000 kg/cm^2 between 0° and 100° C. on resistance in different directions. (3) Elastic Constants. These are much more complicated than thermal expansion or resistance. The trigonal metals have six constants, the tetragonal six, and the hexagonal five. I have determined these constants by measurements of the elastic deformation of properly oriented specimens, and have in addition measured the linear compressibility in two directions to 12000 kg. , which gives information about the behavior under pressure of certain combinations of the elastic constants, and in particular gives the cubic compressibility. It is sufficient to measure the linear compressibility in only two directions, as is the case for resistance and thermal expansion.

The chief difficulty which has prevented the measurement of crystal properties of metals in the past is doubtless that of preparing single crystals of sufficient size. In this paper I first describe in detail the method by which the specimens were prepared (I have already sketched this method in general outline²), then the general methods of making the various sorts of measurements, and then the detailed data for the individual metals.

METHOD OF GROWING LARGE SINGLE CRYSTALS.

The general method is that of slow solidification from the melt. A tubular electric furnace, in a vertical position, is maintained at a temperature above the melting point of the metal in question. The metal in the molten condition in a suitable mold of glass or quartz tubing is slowly lowered through the bottom of the furnace into the air of the room or into a cooling bath of oil. Solidification thus starts at the bottom of the tube and proceeds slowly along its axis, keeping pace with the lowering. If the lowering is at a speed less than the velocity of crystallization and also slow enough so that the latent heat of solidification may be dissipated by conduction, then the metal will usually crystallize as one grain, provided that only one nucleus started in the tube at the bottom. The final casting has of course the cylindrical shape of the mold, not the geometrical form characteristic of the crystalline system of the metal.

It is, possibly, surprising that this method works for all of the metals of the list, because several of them are known to have polymorphic transitions between the melting point and room temperature (tin and antimony). It is evident that on passing through a transition point the same process repeats itself that took place at the melting point.

In applying this method in practise there are various details to attend to. The most difficult and important is to secure the formation of only one grain at the bottom end. This is not always absolutely necessary, and in much of my early work I took no special precautions in this direction and obtained suitable single crystals after cutting off the bottom ends of the castings. The reason is that one orientation of the grains is usually much more favorable for growth than others, so that even if a number of grains start at the bottom, that grain will eventually win through which is most favorably situated. The most favorable orientation is in almost all cases with the plane of easiest



FIGURE 1. The mold used in producing large single crystals.

cleavage or slip parallel to the axis of the casting. This does not fix the orientation of the grain uniquely, since this plane of cleavage may have any orientation within 180° about the axis of the casting, so that a number of grains may start all equally well situated for growth; these grains will then persist throughout the entire length of the casting. To ensure, therefore, a reasonably high percentage of success, one must depend on something more positive than mere chance to ensure the formation of only one original grain. I tried a number of schemes with varying success. The best is to draw the lower part of the mold out into a separate chamber, separated from the main part by a capillary 0.1 mm. or so in diameter, as shown in Figure 1. The capillary acts as a filter, allowing only one of the several grains which may have formed initially in the lower bulb to get through into the main part of the mold. Even this will not always ensure success, because if the grain which gets through the filter is particularly unfavorably situated for growth, a more favorably oriented grain is likely to make its appearance spontaneously at some later stage. To avoid this occurrence as much as possible, one may make the lower chamber fairly long, so that the formation of the most favorably

situated grain may have as much chance as possible to take place below the filter instead of above it.

After the proper starting of the crystal, precautions must still be taken to prevent the appearance of new nuclei, but these precautions are comparatively easy. The most important is freedom from dirt. Specks of dirt clinging to the side of the glass are likely to start new grains. The most likely dirt is small particles of oxide; it is practically impossible to melt a piece of metal which has once solidified and come in contact with the air without the appearance of specks of oxide, even if the melting is performed in vacuum. In order to obtain the molten metal clean, I usually melted the metal in an ante-chamber before the mold proper, separated from the mold by a narrow capillary, which acts as a filter to remove solid dirt. Figure 1 will suggest the general method of procedure. The metal in sufficient quantity is first placed in the ante-chamber *A* through the open mouth of the mold, which is then drawn down at the top end *B* and a glass tube attached by which connections may be made with rubber tubing to vacuum. The mold is now placed in the furnace, the chamber *A* projecting beyond the upper end of the furnace; the mold is evacuated through *B* by a rotary oil pump with which it remains in connection, and the furnace is brought to temperature. The furnace with the mold in it is then brought to a horizontal position by rotating about a suitable axis on which it is mounted, so that now the ante-chamber with the unmelted metal projects in a horizontal position from the furnace. The metal is now melted by an auxiliary gas flame, and raised to a temperature somewhat above that of the furnace. By tipping the furnace, the metal is washed back and forth in *A*. This is an important operation, because in this way large quantities of occluded gas may be eliminated, which otherwise separate during solidification and give an imperfect casting. Some metals are much worse than others in this respect; bismuth particularly is bad, and it may be necessary to manipulate the molten metal for an hour or more before all the gas bubbles have disappeared. After getting rid of the gas, the furnace is rotated back to the vertical position, and the metal allowed to filter through into the mold, admitting air to the antechamber to hasten the filtering. It is well to choose such a quantity of metal that it finally stands a little above the passage from *A* to *C*, thus keeping any oxide on the upper surface and out of the final mold. The glass tube at *B* is sealed off, to prevent further access of air and continued oxidation. Solidification is now started by lowering the mold.

In addition to the complete removal of dirt, the chance formation

of new grains is hindered by a proper design of the mold; a too obtuse taper above the lower capillary may start new grains, probably because the temperature does not change uniformly at such a taper.

The proper speed of lowering depends very much on the metal and the size of the mold. In general, the speeds appropriate to this method are very much less than those used in drawing wires out of the surface of molten metal, as would be expected because of the action of the glass walls in restraining the attainment of temperature equilibrium. In general, for castings as large as 2.2 cm. in diameter, which I have made a number of times and which were the largest allowed by the dimensions of the furnace, a speed as low as 4 mm. an hour is desirable, while for small castings I have used speeds up to 60 cm. per hour. It is in general true that it does no harm to err on the side of too great slowness, but this does not seem to be true for bismuth and tellurium, for which there is doubtless a rather definite optimum speed for any given diameter and external conditions.

It is important that air drafts be kept from the emerging mold, as otherwise new centers of solidification may be started. To avoid drafts the mold may be lowered into a pipe closed at the bottom end, with its upper end tightly pressed against the lower end of the furnace. If cooling in an oil bath is preferable to cooling in the air, as it is for cadmium, the pipe may be filled with oil, and a drip supplied at the upper end to remove the oil displaced by the emerging mold.

The removal of the final casting from the mold is important. If the glass and metal are perfectly clean, the metal will stick and cannot be got out. To avoid this the tube must first be greased. A convenient way to do this is to flush the tube with a heavy mineral oil (Nujol) and then to wash this out with several fillings of petroleum ether, finally heating the tube in an inverted position with a gas flame, working from the top down, driving the film of oil before the flame. It will be found that a sufficient amount of oil clings to the glass to prevent the metal from sticking, but it is otherwise imperceptible in amount. The metal may be removed from the mold by cracking off the glass between the jaws of a vice, having first thoroughly scratched the outside of the glass with a diamond, or better, if greater precaution is necessary, by scratching, and then very rapidly heating the outside of the glass locally in a fine oxy-gas flame, and plunging the tube into water, repeating until the glass is completely cracked off. In any event, the removal from the mold must be made with very great care for the soft metals, of which cadmium is the softest of the above list.

Pyrex glass was used for all the metals above, except antimony, which melts at a temperature above that at which pyrex will stand a vacuum. For antimony I first used quartz, and I have to express my great obligation to Mr. E. R. Berry of the Research Laboratory of the General Electric Co. at Lynn for providing me with the quartz, but I later found that a Scotch combustion tubing is sufficiently rigid at the melting temperature, although considerable care is necessary in its manipulation.

The temperature of the furnace is not a matter of much importance, as would be expected with the slow rates of lowering used here. In order to avoid difficulties from a too fine adjustment of temperature, I usually operated 50° or 100° above the melting temperature. The furnace was run from a rotary transformer attached to the municipal power line. Under the particular conditions of this laboratory this proved to be much more constant than any storage battery available. No regulation, other than the initial regulation by rheostats, was attempted. Slow fluctuations of temperature are not of much importance, and rapid changes are eliminated by the thermal inertia of the furnace.

The lowering was by electric motor, working through worm wheels and various gears to give the range of speed desirable. Detailed description of this part of the apparatus is not necessary.

Contrary to my expectations, it turned out that for many purposes castings of small diameter are better than large ones. In fact it is to be emphasized that in most of this single crystal work the specimen should be brought to the final form with as little mechanical work done on it as possible, the reason of course being the extreme plasticity of some of these metals, and the extreme brittleness of others. In making castings smaller than the maximum allowed by the furnace, various devices were adopted for casting a number at a time, thus saving time. Rods 6 mm. in diameter were cast four at a time in tubes sealed to the bottom of the ante-chamber, each 6 mm. tube having its own bulb and filtering capillary at the lower end. Rods 2.5 mm. in diameter were cast sometimes in groups of 25 or more, each individual tube being provided with its own bulb and capillary filter at the lower end, the group of 25 tubes being mounted within a single large containing tube and filled barometer-wise in an inverted position. Devices of this sort will readily suggest themselves. The difficulty with small diameter castings is in getting rid of occluded gas, which may, if not removed, sometimes segregate itself in bubbles large enough to cut entirely across the diameter of the tube.

Incidentally, this method of production of crystals achieves one very desirable end in that it automatically purifies the metal, those impurities which depress the freezing point segregating themselves in the upper end of the casting. Professor Saunders was kind enough to make some spectroscopic examinations, and he always found the lower end of the casting purer than the upper end. Considerable quantities of impurity may be eliminated in this way, as I found by intentionally adding an impurity of lead to tin. The high values of the temperature coefficients of resistance of the metals used here and their low specific resistances are evidence of their unusually high purity.

The principal particular in which this method requires further development is in some precise method of control of the orientation of the casting. No positive control was attempted in this work, but a large number of castings were made, and those were selected which most nearly satisfied the requirements. It has been already mentioned that the favorite method of growth is with the principal cleavage plane parallel to the axis of the casting. This orientation was very exactly attained in a number of instances; in the larger castings of antimony, for example, no specimens were found which were oriented in any other way. More oblique incidences are favored by small diameter of the casting and by rapid cooling, so that some degree of control is possible in making a large number of castings, but I have no method of control over any particular individual. It would doubtless be possible to attain such a control by inoculating with a piece previously crystallized selected to have the proper orientation, but with the particular forms of apparatus which I used no simple method of doing this presented itself, and it seemed simpler to make a large number of castings and choose the best.

Having made the casting, it is necessary to determine whether it is really a single grain, and if it is, what is the orientation with regard to it of the crystallographic axes. This is almost as difficult as the production of the single crystal itself, and many attempts were made to find a simple and rapid method. Of course X-ray analysis would give the information desired, but this is prohibitively long and complicated. The method finally adopted was the simplest possible, and consists merely in an examination of the appearance of the casting in a bright beam of parallel light. The surface of the casting as it comes from the mold is covered with microscopic or sub-microscopic pits whose sides are the plane faces of the natural crystal, the pits thus constituting negative crystals. These plane faces reflect the light

regularly in definite directions. If the casting is a single grain the entire surface will flash into illumination simultaneously at particular orientations as it is rotated in a beam of light, whereas if there is more than one grain, the different grains flash out separately. The appearance is much like that of the separate grains of an etched metal under a high power microscope. To make this analysis, it is for some metals necessary to examine the casting immediately after removing the glass, as otherwise the surface becomes tarnished. Etching a tarnished surface will sometimes restore the possibility of the detection of the individual grains, but the original cast surface is always far preferable.

The location of the crystallographic axes may most easily be made by means of the reflection pattern. By determining all the positions of regular reflection, the surfaces of the negative crystals are determined, and so from crystallographic data the axes may be found. The method used in locating the positions of regular reflection is a very simple one, for the general idea of which I am indebted to Dr. Langmuir. The source of light is most simply a nitrogen filled lamp in the ceiling of a high studded and partially darkened room. The crystal rod whose axes are to be located is threaded through a wooden sphere, to which it is attached by the light friction of a roll of paper, or by a touch of wax. The rod is now held in the hands at arm's length toward the floor and rotated until a regular reflection flashes out. The orientation with respect to the beam of light is now marked on the sphere by the following device. A piece of plane mirror, the back of which is smeared with a little printer's ink, is held in one hand, the other maintaining the rod in the position of regular reflection, and the mirror rotated until the source of light is also visible in it. The mirror is now touched lightly to the sphere, the ink on the back side marking the position.

From the complete reflection pattern, determined in this way, the location of the axes may at once be found in terms of known crystallographic data. The details of this pattern will be given under the description of the individual metals. The only caution necessary in connection with the method is to avoid marking positions due to double reflections. Such double reflections can at once be identified, if one is on the lookout for them, because they are not confined to a single direction, but occupy a two dimensional locus. I owe this suggestion to Dr. I. C. Gardner.

Before this final method of location of the axes was adopted, a number of other methods were tried, some of which have interest for

their own sakes. For example, much information may be obtained from the manner of mechanical deformation. The impression made by a steel sphere, as in the Brinell test, is not round, but shows the characteristic symmetry of the crystal. Tin shows a four sided impression, and bismuth a three sided. By studying enough of these impressions, on differently oriented surfaces, the axes may be located. The depth of the depression also varies on different faces. Another deformational method, better in some respects, is to make the depression with a chisel edge loaded with a fixed weight. The width of the depression varies characteristically with the orientation of the edge, as well as with the orientation of the surface which receives the impression. The flow figures thrown up by the chisel edge at the ends of the impression furthermore yield a good deal of information. I have also tried determining the variations of scratch hardness, both on different surfaces, and in different directions on the same surface. This method also may doubtless be made to yield the necessary information, but it is more complicated, and gives reproducible results less easily. Since it has been a matter of controversy, however, I may record that I have found perfectly measurable and comparatively large differences of scratch hardness on the same crystal face, and also distinct differences between different crystal faces.

A more rapid method of examination, sufficient for many purposes, is to cut from the crystal a short cylinder, true the flat faces, and compress to plastic flow between polished steel plates. The manner of flow will show whether there is one grain, and will also locate the plane of easiest slip, which is usually perpendicular to the principal axis, and is all the identification of direction necessary for resistance or thermal expansion measurements, or for many measurements of the elastic constants.

If the metal shows easy cleavage, as do zinc, bismuth, antimony, and tellurium, the simplest method is to first check the existence of only one grain by the optical method, and then to locate the plane of easiest cleavage by chipping the corners of the castings. The planes of easiest cleavage give the axis of 6 or 3 fold symmetry. If it is necessary to locate more definitely the other axes, the secondary cleavages may be employed.

The optical method is, however, obviously immensely superior to any of the deformational methods alone, for not only is it rapid and does it give the complete crystallographic orientation, but it does not involve the destruction of any part of the specimen.

METHODS OF MEASUREMENT AND COMPUTATION.

Thermal Expansion. The specimens to be measured were usually in the form of cylinders approximately 2.5 cm. long and 6 mm. in diameter. These were mounted in a steel apparatus, and the temperature of the apparatus and the specimen were changed together, so that effectively the difference of expansion between the steel and the specimen was measured. The differential expansion was determined by means of an optical lever. The mirror was mounted on a knife edge arrangement with an effective length of about 0.4 mm., and the scale was placed at a distance of 4 m., thus giving a magnification of 20,000. The telescope was placed close to the mirror, instead of near the scale as usual, thus doubling the size of the image and making very much easier its location.

The temperature was controlled by means of water baths, rapidly stirred. The specimen in the steel holder was attached to a heavy steel bracket, and the water bath was so arranged that it could be raised from below in a few seconds into position about the specimen. The dimensions of the apparatus were small, and the stirring was rapid, so that temperature equilibrium was attained in less than three minutes after adjusting the bath. Two baths were used, one five degrees above and one five degrees below room temperature. The measurements consisted of a number of readings with the two baths alternately at as short intervals as allowed by the equilibrium requirement. No thermostatic regulation was attempted, but the temperature of the bath was recorded corresponding to each measurement. The mean of a number of such readings gave the data for the calculation of thermal expansion. There was a perceptible drift in the readings due to changes of room temperature. The effect of this may be made to disappear from the average by taking an odd number of readings and operating at regular time intervals. In any event, the effect of drift is comparatively small.

It was necessary to design the apparatus with some care in order to avoid error from unequal expansion in that part of the supporting bracket which projects through the surface of the water. This was attained by so mounting the mirror that the only motion transmitted to it through the surface of the water was the rotation of the shaft attached to the knife edges, which were below the surface of the water, the shaft leaving the surface of the water at right angles. A previous attempt to mount the knife edge above the water was a complete failure.

In using the apparatus it is necessary to know both the magnification of the optical lever, and the absolute thermal expansion of the steel of which the holder is composed, which enters by difference into the final result.

The dimensions of the knife edge mounting for the mirror were determined by producing a known amount of motion with a micrometer screw attached to a vernier head, and measuring the motion of the scale. It was very nearly the same arrangement as I have used previously in calibrating the lever of the linear compressibility apparatus, and the results were gratifyingly regular. The relation between motion of the lever and scale deflection is linear within the range of angles used with a maximum departure of any single reading of not more than $1/4000$, which is good considering the high magnification.

Having determined the optical magnification, the thermal expansion of the steel envelope may be found by measuring the apparent thermal expansion of a single known substance. Fused quartz was chosen for this purpose because of its very low absolute expansion, and therefore the presumably high percentage accuracy of a result into which this quantity would enter by difference. The linear expansion assumed for the quartz was 5.7×10^{-7} . The expansion found in this way for the steel lies in the conventional range of values for ordinary mild steel given in tables of constants.

The calibrating data are now all at hand, so that from the apparent expansion of any of the crystal specimens the absolute expansion may be calculated. No attempt was made to obtain readings at more than two temperatures, so that any variation of thermal expansion from constancy cannot be detected by these measurements.

In the following the usual notation is adopted for the thermal expansion: α_{11} is the linear expansion parallel to the six-, three-, or four-fold axis, and α_1 is the linear expansion in any direction at right angles.

Electrical Resistance. The specific resistance was determined in several ways, some involving cutting specimens from a larger crystal in definite orientations, but the simplest, and the one most often used, involved merely the measurement of the resistance of a long cylindrical casting, the length being so great compared with the cross section that any deviation of the lines of flow from uniformity and rectilinearity could be disregarded. The disadvantage of this last simple method is that the orientation of any single specimen cannot be controlled, but a considerable number of specimens must be used of as wide a range of orientation as may be obtained, and then

by plotting all the results against the orientation the most probable resistance for the axial and the perpendicular direction may be obtained. It is a further disadvantage that the natural castings are not always geometrically perfect; error from this effect is not important, however. The great advantage of the method is that the specimens have been subject to no machining, so that one may be confident that there has been no alteration of the original crystal structure.

The resistance of the unmachined cast rods was determined by a potentiometer method, and in fact the same electrical measuring apparatus was used which I have previously described and used for determining the effect of pressure on the resistance of specimens of small absolute resistance. For many of the measurements the two current connections and the two potential connections were mounted together in a frame with an arrangement so that the whole specimen could be slid along beneath them, thus exploring the length of the specimen for uniformity. The dimensions could be measured with sufficient accuracy with a micrometer.

The measurements of the effect of pressure on the resistance of rods of different orientations was made by methods previously used and already sufficiently described.⁴ The current and potential terminals were in most cases attached to the specimen by soldering, the ratio of length to diameter being sufficient so that no error was introduced by end effects.

In addition to these measurements on natural castings, two methods were attempted for measuring the resistance of machined specimens, which perhaps have sufficient interest to warrant some description. The first of these methods employed a cylindrical specimen, about 1 cm. long and 3 mm. in diameter, turned accurately cylindrical with flat ends. The specimen was soldered with low melting solder at the two ends between two cylindrical copper rods of the same diameter, the whole being carefully made so that there were no irregularities in the external surface. Current was passed in and out at the two ends of the copper, and the potential drop over the middle 2 mm. of the specimen was taken off with needle points pressed against it. If the specimen is machined so as to lie along the crystallographic axis, or at right angles to it, the lines of current flow are straight, and the measurements give immediately the specific resistance. When mounted in a rapidly stirred bath of kerosene to avoid thermal currents, this method is capable of considerable precision, but the difficulty arising from the necessity of careful machining and the ac-

companying danger of damage to the crystal structure did not justify its extended use, and it was in fact used only with tin and zinc.

The second method attempted to measure the resistance of a massive specimen, on which it was necessary to machine only a single flat surface of the order of 1 cm. in diameter. The method consists in pressing against the surface four needle points mounted in the same straight line at fixed distances apart, using the two extreme needles as current terminals and the two inner points for potential terminals. The points must be close together (extreme points 6 mm. apart in the form used) and the specimen large enough so that the flow is essentially that in a semi-infinite solid. The mathematics involved in the use of the method has some interest, and gives a result somewhat paradoxical at first sight. The apparent resistance measured in this way is greatest for that orientation of the four points which lies along the direction of least specific resistance. If R_x , R_y , R_z are the apparent resistances when the line of points is directed along the x , y , and z axes (using surfaces of different orientations if necessary), then the specific resistance along the x -axis is given by

$$\rho_x = \text{Const} \frac{R_y R_z}{R_x},$$

with analogous formulas for the other directions. If the axis of rotational symmetry lies in the surface, measurements on a single surface suffice.

If the flow is two dimensional (thin sheet) instead of three dimensional, it may be shown that the apparent resistance is independent of the orientation of the four points, no matter how great the variation of specific resistance in different directions. The analysis for the two dimensional case has been used in another paper⁵ in connection with measurements of the effect of tension on resistance. The three dimensional analysis is mathematically similar, and it is not necessary to give the details here.

An apparatus was constructed on this principle, and measurements with it verified the mathematics, and gave values for the specific resistance agreeing in general with those found by other methods. It appeared, however, that crystalline disorientation due to machining is a particularly important source of error here, as may be expected from the small dimensions of the apparatus and the fact that the current is thereby confined to the immediate vicinity of the surface. The method was applied to bismuth, cadmium, zinc, and tin. In all cases the machining must be done with extreme care, and since one

cannot be sure of the result unless verified by other methods, I abandoned it as a serious method of crystal measurement. It would seem, however, that the method may have uses with other metals whose crystal structure is less likely to damage, on occasions when it would be convenient to obtain the specific resistance of a massive specimen of an isotropic metal merely by pressing four points against it and measuring a potential drop.

The resistances obtained by any of the above methods usually require to be reduced to values of more immediate significance. Thus in measuring the resistance of long cast rods we obtain the specific resistance in directions which are inclined to the principal axis. We need to know the connection between the resistance in any direction and the two principal resistances along the axis of rotational symmetry and any perpendicular axis. In measuring the effect of pressure on resistance, we measure with terminals fixed to the specimen, which undergoes deformations under pressure. The coefficients obtained under these conditions we call the coefficient of "measured" resistance. We desire to find from the coefficient of "measured" resistance the pressure coefficient of "specific" resistance, that is, the effect of pressure on the resistance of a piece of metal of invariable shape. The same remarks apply to the temperature coefficient of resistance. We ordinarily determine the "measured" temperature coefficient; we require to find the "specific" temperature coefficient. Finally, in comparing the results found here for single crystals with those of other observers for aggregates of crystals we must know how to find the resistance of a haphazard aggregate in terms of the principal resistances of the individual crystals.

We denote by ρ_{11} the specific resistance parallel to the axis of three-, four-, or six-fold symmetry (which will always be taken as the z axis), and by ρ_{\perp} the specific resistance perpendicular to that axis. We further shall always denote by θ the angle between any specified direction and the z axis.

Voigt⁶ has shown that the resistance in any direction in terms of the principal resistances is given by

$$\rho_{\theta} = \rho_{11} \cos^2 \theta + \rho_{\perp} \sin^2 \theta. \quad A.$$

He has also obtained the relation between the resistance of a haphazard aggregate and that of the individual grains

$$\frac{1}{\rho} = \frac{1}{3} \left[\frac{2}{\rho_{\perp}} + \frac{1}{\rho_{11}} \right] \quad B.$$

Next consider the connection between the temperature coefficient of specific resistance in any direction and the temperature coefficient of specific resistance along the axes. Denote by $\rho_\theta(t)$ the specific resistance at temperature t in direction θ , and by β_θ the temperature coefficient of specific resistance in the direction θ . Then by definition of temperature coefficient we have

$$\rho_\theta(t) = \rho_\theta(0) [1 + \beta_\theta t].$$

By relation A we have

$$\left. \begin{aligned} \rho_\theta(t) &= \rho_{11}(t) \cos^2 \theta + \rho_1(t) \sin^2 \theta \\ \text{and} \quad \rho_\theta(0) &= \rho_{11}(0) \cos^2 \theta + \rho_1(0) \sin^2 \theta. \\ \text{Also} \quad \rho_{11}(t) &= \rho_{11}(0) [1 + \beta_{11} t], \\ \rho_1(t) &= \rho_1(0) [1 + \beta_1 t]. \end{aligned} \right\}$$

Substituting now these four relations into the preceding equation gives

$$\beta_\theta = \frac{\rho_{11}(0)\beta_{11} \cos^2 \theta + \rho_1(0)\beta_1 \sin^2 \theta}{\rho_{11}(0) \cos^2 \theta + \rho_1(0) \sin^2 \theta} \quad C.$$

The relation between the temperature coefficients of resistance in different directions is therefore more complicated than that between the specific resistances themselves. An examination of the derivative shows that between $\theta = 0^\circ$ and $\theta = 90^\circ$ β_θ either continually increases or continually decreases. Its rate of change vanishes at $\theta = 0^\circ$ and is a maximum at some intermediate point not in general at 45° .

It is obvious that exactly the same analysis and the same equation C applies, replacing β by γ , the *pressure* coefficient of resistance.

We now have to consider the connection between the coefficients of measured and specific resistance. We discuss first the pressure coefficient. There are two sorts of deformation under pressure to consider, that due to change of length and cross section of the rods, and that due to change of angle between the rod and the z axis. Consider a rod originally of unit length inclined at θ to the z axis. Under a uniform hydrostatic pressure p the projections of the rod along x and z , which were originally $\sin \theta$ and $\cos \theta$ become $\sin \theta [1 - p(s_{11} + s_{12} + s_{13})]$ and $\cos \theta [1 - p(2s_{13} + s_{33})]$ respectively. (See the following section on elastic constants if the notation is unfamiliar.)

We find from this that for unit pressure the decrease of length is

$$-\frac{\Delta l}{l} = \cos^2 \theta (2s_{13} + s_{33}) + \sin^2 \theta (s_{11} + s_{12} + s_{13}).$$

But the decrease of volume is

$$-\frac{\Delta V}{V} = 2(s_{11} + s_{12} + 2s_{13}) + s_{33}.$$

Now the cross section decreases by $-\left(\frac{\Delta V}{V} - \frac{\Delta l}{l}\right)$. Hence due to change of dimensions only, the resistance would increase by $-\left[\left(\frac{\Delta V}{V} - \frac{\Delta l}{l}\right) - \frac{\Delta l}{l}\right]$, or

$$2s_{11} \cos^2 \theta + 2s_{12} \cos^2 \theta + 2s_{13} \sin^2 \theta + s_{33}(1 - 2 \cos^2 \theta) \quad D.$$

For those metals whose resistance decreases under pressure, the pressure coefficient of measured resistance is to be increased numerically by D in order to obtain the pressure coefficient of specific resistance, and conversely with those metals whose resistance increases under pressure.

Now consider the correction arising from change of angle. By taking the ratio of the projections of the rod above we find that under unit pressure the angle θ changes by

$$\Delta \theta = \sin \theta \cos \theta [s_{33} + s_{13} - s_{11} - s_{12}].$$

Now we have

$$\rho_\theta = \theta_{11} \cos^2 \theta + \rho_{11} \sin^2 \theta.$$

Whence

$$\Delta \rho_\theta = 2 \sin \theta \cos \theta [\rho_{11} - \theta_{11}] \Delta \theta,$$

and substituting,

$$\Delta \rho_\theta = 2(\rho_{11} - \theta_{11}) \sin^2 \theta \cos^2 \theta [s_{33} + s_{13} - s_{11} - s_{12}]. \quad E.$$

The resistance changes by this amount because of change of angle; we correct for it by subtracting $\Delta \rho_\theta$ from the measured change of resistance. In general, the correction E is much smaller than D, and is usually just on the edge of the negligible.

Analysis similar to the above applies to the temperature coefficient, replacing $s_{11} + s_{12} + s_{13}$ by $-\alpha_1$, and $2s_{13} + s_{33}$ by $-\alpha_{11}$. We thus find that

$$2\alpha_1 \cos^2 \theta + \alpha_{11}(1 - 2 \cos^2 \theta) \quad F.$$

is to be added to the measured temperature coefficient of resistance to correct for the change of dimensions, and

$$\frac{2(\rho_1 - \rho_{11})}{\rho_0} \sin^2 \theta \cos^2 \theta [\alpha_{11} - \alpha_1] \quad G.$$

to correct for the change of angle, the result obtained after applying the correction being the temperature coefficient of specific resistance in the direction θ .

Experimentally the procedure is usually as follows. The specific resistance is measured in a number of directions, and a curve passed through the points by equation A, from which the best values of ρ_{11} and ρ_1 are obtained. The temperature (or pressure) coefficient of resistance is now measured for two different directions as close as possible to the two axes, and from these results by equations F and G (or D and E) the specific coefficient found in the two directions. These results are now substituted into equations of the type C, giving two equations for calculating the two unknowns β_{11} and β_1 (or γ_{11} and γ_1).

We may find from formula B that the temperature coefficient of specific resistance of a haphazard aggregate is connected with that of the grains by the relation

$$\frac{\beta}{\rho} = \frac{1}{3} \left[\frac{2\beta_1}{\rho_1} + \frac{\beta_{11}}{\rho_{11}} \right], \quad H.$$

with of course a similar formula for the pressure coefficient.

This analysis suggests an interesting possibility with regard to determining the change of the elastic constants under high pressures. By measuring the linear compressibilities we obtain $s_{11} + s_{12} + s_{13}$ and $2s_{13} + s_{33}$ as functions of pressure. Suppose now we measure the effect of pressure on the resistance of rods of four orientations, two of them along the axes. The linear compressibilities enable us to correct the measured coefficients along the axes to specific coefficients. Formula C now enables us to calculate the specific coefficients for the two other directions. But these may also be calculated in terms of the measured coefficients in those directions and the combination of constants $2(s_{11} + s_{12}) - s_{33}$ and $2s_{13} + s_{33}$. Comparison of the two results gives the values under pressure of the last two combinations of constants. One is already known from the linear compressibility, and therefore can be used only as a check, but we have in all, three relations from which the behavior under pressure of

s_{33} , s_{13} , and $s_{11} + s_{12}$ may be found. Probably in practise the accuracy demanded in the measurements would be very high.

Elastic Constants. The linear compressibilities were measured by methods already described and applied to a large number of cubic metals.³ The identical apparatus was used. In general the specimens were machined from a large casting to have a diameter of the order of 6 mm. and a length of 2.5 cm. The proportions are such that there is comparatively little danger of damaging the crystal structure to any depth if the machining is carefully done. The rough rods were usually cut from the large casting with a jeweller's saw by hand, and the machining was done in a jeweller's lathe, run at a high speed and taking a very fine chip. In some cases it was necessary, in order to attain the requisite length, to build up the specimen of two pieces, placed end to end. The same sort of procedure has already been used for other metals, and introduces no error in measurements of this sort, although it does certainly introduce error into other sorts of measurement, as Young's modulus by a compression method, for example. These measurements of linear compressibility are susceptible of a relatively high degree of accuracy, much greater than the measurements of any of the other elastic constants. One reason, of course, is that an elastic limit does not exist for hydrostatic pressure, so that a comparatively large deformation may be produced by high pressures. It is a matter of experiment that the relation between deformation and pressure is linear over so wide a range of pressure that a real increase of accuracy is obtained in this way. There is furthermore a very simple check on the linear compressibility measurements in that the sum of the three linear compressibilities in three mutually perpendicular directions should agree with the cubic compressibility as determined by other methods.

The symmetry of the linear compressibility is the same as that of electrical resistance or thermal expansion, so that only two specimens are necessary, directed along and at right angles to the principal crystallographic axes. Other specimens oriented in different directions would merely give a check on measurements already made.

In discussing further the methods of determining all the elastic constants, it will pay to have before us the detailed relations between stress and strain for the various crystal systems measured here.

For the hexagonal system (zinc and cadmium) there are five constants, and the relation between stress and strain, using the familiar notation of Voigt is:

$$\begin{aligned}
 e_{xx} &= s_{11}X_x + s_{12}Y_y + s_{13}Z_z + 0Y_z + 0Z_x + 0X_y, \\
 e_{yy} &= s_{12}X_x + s_{11}Y_y + s_{13}Z_z + 0Y_z + 0Z_x + 0X_y, \\
 e_{zz} &= s_{13} \quad + s_{13} \quad + s_{33} \quad 0 \quad 0 \quad 0, \\
 e_{yz} &= 0 \quad 0 \quad 0 \quad + s_{44} \quad 0 \quad 0, \\
 e_{zx} &= 0 \quad 0 \quad 0 \quad 0 \quad s_{44} \quad 0, \\
 e_{xy} &= 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 2(s_{11} - s_{12}).
 \end{aligned}$$

For the trigonal system (bismuth, antimony, and tellurium) there are six constants, and the relation between stress and strain is:

$$\begin{aligned}
 e_{xx} &= s_{11}X_x + s_{12}Y_y + s_{13}Z_z + s_{14}Y_z + 0Z_x + 0X_y, \\
 e_{yy} &= s_{12} \quad + s_{11} \quad + s_{13} \quad - s_{14} \quad 0 \quad 0, \\
 e_{zz} &= s_{13} \quad + s_{13} \quad + s_{33} \quad 0 \quad 0 \quad 0, \\
 e_{yz} &= s_{14} \quad - s_{14} \quad 0 \quad s_{44} \quad 0 \quad 0, \\
 e_{zx} &= 0 \quad 0 \quad 0 \quad 0 \quad s_{44} \quad 2s_{14}, \\
 e_{xy} &= 0 \quad 0 \quad 0 \quad 0 \quad 2s_{14} \quad 2(s_{11} - s_{12}).
 \end{aligned}$$

For the tetragonal system (tin) there are six constants, and the relation between stress and strain is:

$$\begin{aligned}
 e_{xx} &= s_{11}X_x + s_{12}Y_y + s_{13}Z_z + 0Y_z + 0Z_x + 0X_y, \\
 e_{yy} &= s_{12} \quad s_{11} \quad s_{13} \quad 0 \quad 0 \quad 0, \\
 e_{zz} &= s_{13} \quad s_{13} \quad s_{33} \quad 0 \quad 0 \quad 0, \\
 e_{yz} &= 0 \quad 0 \quad 0 \quad s_{44} \quad 0 \quad 0, \\
 e_{zx} &= 0 \quad 0 \quad 0 \quad 0 \quad s_{44} \quad 0, \\
 e_{xy} &= 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad s_{66}.
 \end{aligned}$$

The z axis is here the axis of six-, three-, or four-fold symmetry. The x and y axes, at right angles to the z axis, are determined in a way which will be further specified when necessary under the description of the individual metals.

Physically the constants fall into three different groups. We may call the "rectangular" constants those whose subscripts are any combination of the numbers 1, 2, 3. These constants give the strains of elongation produced by stresses which act normally to their planes. The "shearing" constants are those whose subscripts are combinations of the numbers 4, 5, 6. Physically they determine the shearing strains produced by shearing stresses (stresses acting tangentially to their planes). The "cross" constants are the remaining ones, whose subscripts are chosen one from the group

1, 2, 3, and one from the group 4, 5, 6. These constants determine the elongation produced by shearing stresses, or the shearing strains produced by normal tractions. There is only one of these cross constants in the group of metals above, namely s_{14} of the trigonal system. Different methods are necessary in measuring the constants of the different groups.

In selecting the methods for determining these constants I have been guided by two desires; first, to make the method as direct as possible, measuring if possible the various constants directly instead of various combinations of them, and secondly, to obtain check measurements as abundantly as possible. Obtaining checks is of considerable importance if one is to have confidence in the results.

We first consider the rectangular constants. The arrangement of these is exactly the same for the three crystal systems, and the same methods of measurement apply to all. It is in the first place evident that the linear compressibilities give the two combinations $s_{11} + s_{12} + s_{13}$ and $2s_{13} + s_{33}$. The cubic compressibility is given by the combination $2(s_{11} + s_{12} + 2s_{13}) + s_{33}$. To completely determine the rectangular constants we need two more relations. The simplest method is to determine the constants directly. Thus it is evident that if a specimen is cut lying along the x axis and is subjected to a simple compression (stress X_x) the longitudinal contraction e_{xx} gives at once the constant s_{11} , and the two lateral expansions e_{yy} and e_{zz} the constants s_{12} and s_{13} . This was in fact the method adopted in many cases. Here the advantage of procuring large single crystals is evident, because it permits the use of specimens large enough to measure the lateral expansions. This has seldom been done previously, even by Voigt in measuring many non-metallic crystals. It is evident on examining the equations that for this kind of distortion there is rotational symmetry about the z axis, so that measurement of the three strains on any rod cut at right angles to the z axis gives directly the three constants, and it is not necessary to locate the x and y axes, but only the z axis. The remaining rectangular constant s_{33} may be obtained by a measurement of the longitudinal contraction under a compressive stress Z_z applied to a specimen whose length lies along the z axis. The lateral expansion of such a specimen in any direction gives again s_{13} ; there is only one independent lateral expansion for such a specimen. Complete carrying out of the scheme outlined above would thus give eight measurements for the four rectangular constants (including the cubic compressibility of other observers). As a matter of fact this was not usually done because

of the difficulty of preparing a specimen of sufficient size lying along the z axis. The reason for this is that the plane of easiest cleavage or slip usually lies perpendicular to the z axis, so that the specimen is very likely to break or be damaged in preparation. Usually therefore, I have obtained essentially only six measurements for these four rectangular constants, two linear compressibilities, one cubic compressibility (other observers) and three direct measurements under a simple compressive stress X_z . In many cases these last measurements were supplemented by measurements of the extension under tension of a rod lying along the x axis, this rod being the natural casting and unmachined and long enough to get rid of end effects. I did not measure the lateral contraction of these rods under tension. Neither did I attempt the measurement of any of the rectangular constants by the bending of rods. This has been the favorite method, but it is much less direct, and it seemed to me much less desirable in cases like the present where the direct measurements can be made.

The shearing constants involve a shearing stress. Unfortunately there seems no simple mechanical way of applying a simple shearing stress analogous to the simple normal tractions which may so easily be applied in measuring the rectangular constants, and a more indirect method has to be used. The best is without doubt the usual method of measuring the twist of a cylindrical rod under a torque. The method is more or less indirect because the state of strain is not uniform throughout the rod, but is greatest at the outside surface and least at the inside. The formulas are comparatively simple, however, and the results of measurements are not open to much question if the material is homogeneous, as it must be in the case of these crystals. The amount of twist of a rod of given dimensions under a given torque depends on the orientation of the rod with respect to the z axis, and in general involves all the elastic constants. The formulas are given in Voigt's book. The specimen is chosen by preference so that the combination of constants is as simple as possible.

For the hexagonal and trigonal systems there is only one independent shearing constant s_{44} , and a single observation of the twist of a rod of known orientation suffices to determine it. The most convenient orientation is with the z axis perpendicular to the length of the rod, (principal cleavage plane parallel to the length) and in this case the torsion constant is given by $s_{11} - s_{12} + \frac{1}{2}s_{44}$. Since s_{11} and s_{12} are supposed already known, the constant s_{44} may at once be found. If it were possible to observe the torsion of rods whose length is parallel to the z axis, the constant s_{44} could be obtained directly

without connection with the other constants, but it has already been explained that the preparation of such rods is usually difficult (except in the case of tellurium for which it is easiest). The first method does not lead to a bad value for s_{44} , however, because the constants s_{11} and s_{12} are usually considerably less than s_{44} , so that although s_{44} is obtained by difference, the difference involved is not the difference of two numbers closely equal to each other. A check on the value of s_{44} is given by torsion measurements on rods of other orientations or by repeating the measurements on several rods of the same orientation. A number of such check measurements were usually made, the details of which will be given under the separate metals.

The tetragonal system differs from the others in having two independent shearing constants. These must be determined by torsion observations on rods of two different orientations, and the check measurements by observations on still other orientations. There is an inconvenient complication here in that it is necessary to know the orientation of the x and y axes in addition to the relative position of the z axis and the axis of the rod. The details will be given later.

There is only one cross constant among the metals measured here, s_{14} of the trigonal system. Its measurement is complicated. Direct measurement on a specimen cut so as to lie along one of the crystallographic axes would involve the measurement of an extension under a shearing stress or a shear under a normal traction, neither of which can conveniently be made on small specimens. An indirect method is therefore necessary. The simplest method seems to be the measurement of the longitudinal extension under tension of a rod cut at an angle other than 0° or 90° with the z axis. The formulas given by Voigt show that in general under such conditions the extension involves the constant s_{14} . The orientation of the x and y axes also enters the result. For one direction of orientation the effect of s_{14} on the extension may be a maximum, while for a change of orientation of only 30° the effect disappears entirely. With a period so short one would expect the influence of s_{14} at best to be comparatively slight, and it is in fact difficult to determine accurately under the best conditions, being given by the difference of numbers nearly equal. Furthermore, the best conditions are rather exacting, and among a large number of castings I found only a few that were suitable for the attempt. A check on the values of s_{14} is given by observations on different specimens at different orientations.

Experimental Methods of Measuring Strain. There was nothing especially novel in the methods employed. The general method for

measuring changes of length, either longitudinal or transverse, was some adaptation of the rocking knife edge with mirror and scale. High magnifications were usually necessary, which for the transverse expansions sometimes rose to 1.2×10^5 . Various arrangements for loading, either direct or through a lever, were adopted, depending on the dimensions of the specimens. Transfer pieces of varying dimensions were used for transferring the change of length to the rocking lever. In measuring the change of length, the shortest effective length employed was 0.4 cm. and the longest 10 cm. The transverse expansions were usually measured on pieces 6 mm. or 1.2 cm. in diameter.

Considerable difficulty was experienced in measuring the longitudinal compression under a one-sided compressive force. Short specimens are necessary, as long ones will buckle. There is considerable difficulty with short specimens because of the necessity of perfect end conditions. I was not successful in compressing a specimen with flat ends between plungers with flat ends in spite of extreme care in machining both the specimens and the plungers. The method by which success was attained was to cement with a very small amount of soft cement to each end of the specimen a cylindrical steel block, accurately concentric with it, in the center of the other side of which was a depression for a small steel ball (1.6 mm. in diameter), which rested also in a depression in the center of the plunger. In this mounting the specimen is free to adjust itself for any irregularities, and consistent results were obtained. The plungers, of course, must be rigidly held to avoid side play.

The twist was measured with an instrument of obvious design. The torque was applied through an arm working practically without friction on knife edges, and the amount of twist was measured with two telescopes and scales set on mirrors attached to the two ends of the specimen.

In all cases the deformation was measured between actual points situated on the specimen. Early attempts to measure the deformation between points not on the specimen itself, as by measuring the longitudinal compression by measuring the approach of the steel plungers with which the compression was produced, were a failure. Attempts were also a failure to utilize specimens built up of two pieces, although this is possible in measuring linear compressibility under hydrostatic pressure or thermal expansion, there being in these cases no change of stress across the opposing surfaces.

Due regard was paid to the question of end effects, and the measur-

ing appliances were always situated far enough from the ends to avoid error from this effect.

In all these measurements the most easy source of error arises from exceeding the elastic limit of the crystal, which is often unbelievably low. Care must be taken that the measuring instrument itself, where applied to the specimen, does not locally exceed the elastic limit. This was a particular source of trouble in measuring the transverse expansion. In the early devices for this measurement, motion was transferred to the mirror by steel points pressed against the specimen. The points had to be replaced by flat bearing surfaces of steel, maintained in position parallel to themselves by arrangements which need not be described here in detail.

DETAILED DATA.

Tungsten. Tungsten belongs to the cubic system, and therefore properly does not belong within the range of material intended here. But since I was fortunate enough to obtain a good crystal and the measuring devices were already developed, the opportunity was not to be lost. Being cubic, the properties of tungsten are of special simplicity. The main questions are whether the properties of the single crystal differ appreciably from those of the drawn wire on which most measurements have been made, and what are the *three* elastic constants.

I owe the crystal to the kindness of Dr. Langmuir of the General Electric Co. who obtained it from the German General Electric Co. It was in the form of a rod 7 or 8 cm. long and 7 mm. in diameter. It had been recrystallized from the sintered rod by heating in vacuum for several hours to a temperature near the melting point. When heated in this way for a long time, recrystallization starts at some point and proceeds rapidly until the entire rod is converted into a single crystal grain, except the extreme ends which are in contact with the supports. After recrystallization, the surface of the rod was etched by the admission of a slight amount of water vapor to the vacuum chamber, thus bringing out the crystal structure. By the optical test the axes could be readily located. The reflection pattern is that of the dodecahedral faces corresponding to the edges of the fundamental cube. The orientation was such that ten of the twelve faces could be identified; the angles of reflection corresponding to the other two faces were unfavorable. For the measurements contemplated it was necessary to completely determine the location of all

three cubic axes. The dodecahedral faces are designated as (1 1 1) and (1 1 0) faces. This fixes the x , y , and z axes with respect to the reflection pattern. The z' axis was chosen along the axis of the cylinder, and the x' and y' axes arbitrarily at right angles. The scheme of angles for this crystal is as shown.

	x	y	z
x'	90°.0	87°.0	3°.0
y'	29.0	61.0	89.0
z'	61.0	29.6	87.5

In deriving this scheme all nine angles were independently measured, and then such readjustments made as were necessary to satisfy the orthogonality conditions. Four of the nine angles were readjusted, the maximum change being 2.5° and the average change (for the four) 1.4°.

After determining the orientation, the crystal was ground to a geometrically perfect cylinder. This was necessary because the rod was bent somewhat, having sagged between the electrodes during the heating before recrystallization. Of course the crystal structure was linear, independent of the curvature of the rod. The grinding destroyed the reflection pattern, so that it was necessary to determine the pattern before grinding.

The linear compressibility was measured in the regular way with the apparatus which in my previous description I have designated as the lever apparatus for long specimens. The length of the finished cylinder was 6.3 cm. The measurements were entirely satisfactory, and show as much accuracy and consistency as any of the compressibility measurements by this method, and this is in general a tenth of a per cent or better. The linear compressibility was found at 30° and 75°, from which the volume compressibility is:

$$\begin{aligned}
 -\frac{\Delta V}{V_0} &= 3.18 \times 10^{-7}p - 1.4 \times 10^{-12}p^2 && \text{at } 30^\circ \\
 &= 3.18 \times 10^{-7}p - 1.5 \times 10^{-12}p^2 && \text{at } 75^\circ,
 \end{aligned}$$

the unit of pressure being the kg/cm².

Tungsten belonging to the cubic system has only one independent linear compressibility, so that this is all the information about the

three elastic constants that can be obtained by measurements under hydrostatic pressure.

These results for compressibility may be compared with results previously found. The result for the single crystal agrees within 1% with that previously found for drawn wire of high density, the compressibility of the crystal being slightly greater. Not only is the initial compressibility the same as found before, but the second degree term is also nearly the same.

Other relations between the elastic constants were obtained by the following measurements: (1) Longitudinal compression under a one-sided compressive stress applied lengthwise of the rod. The constant for this deformation, that is the longitudinal compression per unit length per unit stress per unit area, is designated by Voigt by s_{33}' , who gives the general formulas from which the special value for the cubic system in terms of the direction cosines and the three principal elastic constants may be deduced. (2) Lateral contraction under longitudinal compression along the x' and y' axes. These constants are designated by Voigt by s_{12}' and s_{13}' , and the formulas are given. (3) Torsion about the axis of the cylinder. The constants for this deformation (twist per unit length, etc.) is designated by Voigt by $s_{44}' + s_{55}'$; the special value for the cubic system may be found from Voigt's formulas. Substituting now into the equations derived from Voigt the experimental values for the constants for the various directions and the numerical values of the direction cosines, and using the results found for the linear compressibility in dyne units, gives the following set of five equations to determine the three elastic constants.

- (1) $s_{11} + 2s_{12} = 1.082 \times 10^{-12}$,
- (2) $.636s_{11} + .364s_{12} + .182s_{44} = 2.54 \times 10^{-3}$,
- (3) $.359s_{11} + .640s_{12} - .179s_{44} = -8.39 \times 10^{-14}$,
- (4) $.0038s_{11} + .977s_{12} - .002s_{44} = -7.14 \times 10^{-14}$,
- (5) $1.456(s_{11} - s_{12}) + 1.272s_{44} = 13.0 \times 10^{-13}$.

These equations are not entirely consistent, and we have the problem of the best method of determining the most probable value of the constants. The method I have adopted is to solve equations 1 and 4 for s_{11} and s_{12} (1 is by far the most accurate of the equations and the s_{12} term in 4 greatly preponderates), and then to average the values which these two values give for s_{44} when substituted in the

three remaining equations, weighing according to the coefficient. As a matter of fact, this method had to be applied by successive approximations, first neglecting the s_{11} and s_{44} terms in 4, carrying through the solution as suggested, and then correcting the value of s_{12} by the small correction terms which are given with sufficient accuracy by the first approximation.

The degree of consistency of the measurements, and the accuracy of the final result is to be judged by the closeness with which the equations 2, 3, and 5 are satisfied by the final values. These are the final values adopted:

$$s_{11} = 2.534 \times 10^{-12},$$

$$s_{12} = -.726 \times 10^{-12},$$

$$s_{44} = 6.55 \times 10^{-12}.$$

Substituted in 5 these give 8.34 on the left hand side against 8.25 on the right; into 2, 2.536 against 2.54; and into 3, $-.727$ against $-.839$.

This check is as close as could be expected in view of the accuracy of the readings. The sensitiveness of the readings for an individual determination of a deformation other than a linear compressibility did not correspond to an accuracy greater than 2 or 3%; the mean of ten readings may have possibly improved the accuracy three times.

It is interesting to see how nearly these constants satisfy certain significant relations. In the first place, if the material were isotropic, and characterized by only two elastic constants instead of three, the shearing constants would be connected with the two rectangular constants by the relation $s_{44} = 2(s_{11} - s_{12})$. Substituting the values above for s_{11} and s_{12} gives 6.52 against 6.55×10^{-12} for s_{44} . Hence for this substance it would appear that the isotropic relation is probably satisfied within the limits of error.

In the second place we have the relation known as Cauchy's relation, which has been of considerable historical importance, but is not now to be taken seriously, deduced on the hypothesis that the forces between atoms act in the line of centers. This relation, which is between the elastic moduli instead of between the constants, is $c_{12} = c_{44}$. The moduli may be computed from the constants above by well known equations, and are: $c_{11} = 5.13 \times 10^{12}$, $c_{12} = 2.05 \times 10^{12}$, and $c_{44} = 1.53 \times 10^{12}$. Cauchy's relation therefore fails within a margin considerably greater than the experimental error.

The only other constant determined for this tungsten was its specific electrical resistance. The potentiometer method was used. In order that the current flow might be in straight lines, which would not occur in a specimen of these dimensions if the usual point or single contact electrodes were used, the electrodes were made of flat pieces of copper, amalgamated, and pressed against the ends of the cylinder so as to be in contact over the entire plane ends. The specific resistance at 20.1° C. was found to be 5.48×10^{-6} . This is a trifle lower than the value 5.51 at 20° given by Langmuir for ordinary tungsten wire. The difference is in the direction one might expect, the conductivity of the crystal being better because of the more regular arrangement, but is in the opposite direction from that which might be expected from the difference of density.

Zinc. This metal is very easy to crystallize, and a large number of experiments were made on rods varying in size from 2.5 mm. to 2.2 cm. in diameter. The preferred manner of growth is with the basal plane parallel to the axis of the cylinder. This is in accord with what might be expected, because it is known that the separation of the atoms is greatest along the hexagonal axis, and therefore their density is greatest in the basal plane, so that they might pile themselves into the crystal most rapidly in this direction, the forces being greatest because of proximity. Practically all the castings of 1 cm. or more diameter had the basal or principal cleavage plane within a few degrees of parallel to the axis of the casting, but a number of specimens of the small size (2.5 mm.) were obtained in which the angle of inclination was sometimes as great as 83° . Because of the ease of growing these crystals I did not experiment much with variations in the rate of lowering the mold from the electrical furnace, but confined myself to the slower rates, between 1.6 and 0.4 cm. per hour. Crystals 1 cm. in diameter were readily produced by the more rapid rate, and the only attempt I made at the largest size was successful with the slowest rate.

Zinc from three different sources was used, all supposed to be of high chemical purity. Specially refined zinc from Eimer and Amend, melting point zinc from the Bureau of Standards, and the purest zinc from Kahlbaum. The Bureau of Standards zinc has been used in some of my previous work, and I have given the analysis in detail. The total purity claimed was 99.992 zinc, by difference. I have no special analysis for the Eimer and Amend zinc, but the purity claimed for it is as great as this. It is to be noticed, however, that this analysis does not include the oxide, and there was doubtless more or less

present in both these zincs. I have not the analysis of the Kahlbaum material, but its electrical conductivity was consistently higher than that of the other two varieties, which were in close agreement, and is therefore presumably of higher purity, the difference doubtless being due to oxide. There was no difference evident between zinc from the different sources in other than the electrical properties, and they could be used interchangeably in the elastic measurements. There is however, an obvious difference in properties which were not specially investigated here, namely the phenomena of plastic flow. The Kahlbaum zinc was distinctly more plastic than the other varieties. It is evident that the highest purity is needed here, and that a comparatively slight amount of impurity by acting as "keys" between the slip planes (see Jeffries?) may very materially alter the flow phenomena.

The reflection pattern of zinc is that of a truncated double hexagonal pyramid, the planes which are usually developed being the (0001) , basal, and the $(10\bar{1}1)$ planes. The relative development of the latter depends somewhat on the rate of cooling. Because, however, of the very perfect cleavage of zinc it is possible in many cases to dispense with a complete optical examination. The examination by the cleavage planes is easily made as follows. At each end of the cylindrical casting, within a couple of mm. of the end, a saw cut is made girdling the casting and reaching half way to the center. The flange thus formed is broken through at various places by driving into it a steel point in the direction of the cylindrical axis. Rupture takes place along the cleavage plane. Similar orientation of the cleavage plane at all places gives the criterion for a unique crystal grain, and at the same time the plane locates the hexagonal axis, which is perpendicular to it. It is not necessary in order to determine those properties of hexagonal crystals investigated here to know further the location of the x and y axes with respect to the hexagonal axis, so that the location of the cleavage plane completely suffices.

A fresh metal cleavage surface is a strikingly beautiful thing, and it was possible to obtain them in great perfection from zinc.

Thermal Expansion. The samples used were the same as those whose linear compressibility was also measured. They were of Bureau of Standards zinc, cut from a casting 1.2 cm. in diameter. The specimens whose cleavage plane was parallel to the length was in one piece, but the one with length perpendicular to the cleavage planes was in two pieces. It has already been explained that this introduced no error in such cases as this.

At room temperature, over a mean range of 5° on each side, the linear expansion was found to be:

$$\alpha_1 = 12.6 \times 10^{-6}$$

$$\alpha_{11} = 57.4 \times 10^{-6}.$$

Both of these values are less than those found recently by Grüneisen and Goens,² which are 14.2 and 63 respectively. Their diagram is not altogether clear, however, and would seem to indicate that for another specimen than that for which they made complete measurements the constants may be less.

The extreme difference of the values in the two directions is the feature of chief interest here.

Electrical Resistance. Measurements of the specific resistance were made by the three methods described in the introduction. Of course

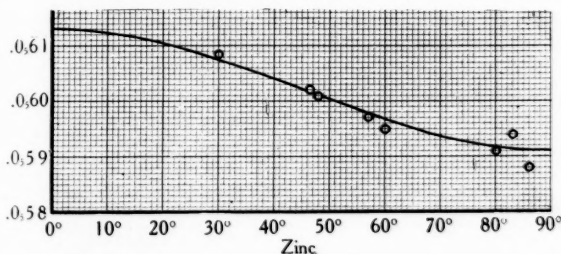


FIGURE 2. The specific resistance at 20° C. of zinc as a function of the angle between the hexagonal axis and the direction of flow.

those on the unmachined castings were the best. Measurements on about forty different specimens were made in all. As already mentioned, the specific resistance of the Eimer and Amend and the Bureau of Standards zinc was consistently higher by about 3% than that of Kahlbaum. The results obtained with Kahlbaum's zinc are the only ones retained in the final results, but the other measurements confirm these in giving the same ratio for the resistance parallel and perpendicular to the axis.

The specific resistances of rods of Kahlbaum's zinc at various inclinations to the axis are shown in Figure 2. These rods were all about 6 mm. in diameter. None were obtained with the cleavage plane more inclined to the cylindrical axis than 55° , but this is suf-

ficient to give the resistance for the 90° inclination by formula A of the introduction.

From this curve the following values may be deduced for the specific resistances at 20° C.:

$$\rho_1 = 5.91 \times 10^{-6}$$

$$\rho_{11} = 6.13 \times 10^{-6}$$

The ratio of the two resistances is 1.036.

The agreement with the values of Grüneisen and Goens is not as close as might be desired. They find for ρ_1 at 20° 5.84×10^{-6} , which does not differ greatly, but for the ratio of the two resistances 1.080. The average resistance for all directions is 5.98×10^{-6} according to my measurements, and 5.99 according to theirs. The difference is small, but is not in that direction which would be accounted for by greater impurity of my zinc. Grüneisen and Goens do not give the details of the sources of their zinc, but at least part of it was Kahlbaum, the same as mine. Neither do they give the details of their measurements of specific resistance, so that we have no means of estimating the probable accuracy of their results.

The temperature coefficient of resistance of three pieces was measured between 0° and 90° , with the following results:

Angle of hexagonal axis with axis of specimen	Average temperature coef- ficient 0° - 100°
7°	0.00422
28.5	.00409
90.	.00412

The source of the $28^\circ.5$ specimen was the Bureau of Standards, whereas that of the other two was Eimer and Amend. Discarding the $28^\circ.5$ observation, the coefficient parallel to the axis appears to be probably about 0.24% greater than at right angles. Unfortunately I have no measurements on the temperature coefficient of the Kahlbaum zinc. The results found above agree well with those of Grüneisen and Goens. who find a coefficient greater by 0.28% along the axis.

The effect of pressure on the resistance was measured on three samples of varying orientation at 0° and 95° C. Two of them were Eimer and Amend's zinc, and the third ($28^\circ.5$) was from the Bureau of Standards. They were rods 2.5 mm. in diameter, and were used

without machining. The conventional potentiometer method was used; the terminals were soldered to the specimens. The total length between potential terminals was from 4 to 6 cm. The measurements were in every respect as good as those which I have previously obtained with non-crystalline samples. The average deviation from a smooth curve of the individual readings with the 7° sample was 0.17% of the total change, with the 28.5 sample 0.20%, and with the 90° sample 0.64%. The following results were obtained:

Angle of Hexagonal axis with axis of Rod	Measured Changes of Resistance	
	0° C. — $\Delta R/R_0$	95° C. — $\Delta R/R_{95}$
7°	$(11.68p - 11.72 \times 10^{-5}p^2) \times 10^{-6}$, $(11.58p - 12.65 \times 10^{-5}p^2) \times 10^{-6}$	
28.5	$(9.965p - 9.41 \times 10^{-5}p^2) \times 10^{-6}$, $(10.127p - 10.86 \times 10^{-5}p^2) \times 10^{-6}$	
90°	$(5.258p - 5.97 \times 10^{-5}p^2) \times 10^{-6}$, $(5.316p - 6.19 \times 10^{-5}p^2) \times 10^{-6}$	

The unit of pressure is here 1 kg/cm². The variations of pressure coefficient with direction are seen to be much larger than those of temperature coefficient of resistance or of resistance itself. The decrease under pressure is greatest parallel to the hexagonal axis, which is also the direction of greatest resistance.

The results above are for "measured" resistance. We may convert these to changes of specific resistance by the formulas of the introduction. Correcting the results at 0° C., we have for the initial pressure coefficients (the second degree term in the pressure coefficient cannot be corrected with the data at hand because we do not know the variation of the elastic constants with pressure):

Hexagonal axis 90° with length	— 6.55×10^{-6}
" " 28.5 " "	— 9.54
" " 7 " "	— 10.80

Using these coefficients of specific resistance at 90° and 7° we find with the aid of formula C in the introduction that the initial pressure coefficient of specific resistance at 0° C. parallel to the hexagonal axis is — 10.87×10^{-6} .

Correcting the temperature coefficients of measured resistance, we obtain the following results:

Temp. coeff. of sp. resis. parallel to hex. axis	0.00419
“ “ “ “ “ perpendicular “ “	0.00418

Within the limits of error, the effect of temperature on specific resistance is probably the same in every direction.

Elastic Constants. The linear compressibility was measured in the regular way with the lever apparatus for short specimens. Measurements were made perpendicular and parallel to the hexagonal axis. Both specimens were machined carefully from a large casting, the diameter of each being about 6 mm. and the length 2.6 cm. The perpendicular specimen was in one piece, but the parallel specimen was in two. It was found that the compressibility perpendicular to the axis is very nearly the same as that of steel. Since the method is a differential method, this means comparatively large irregularities in the measured value of the difference of compressibility, but the compressibility itself should not have any greater percentage inaccuracy than usual for this reason.

Measurements on each of these specimens to 12000 kg. at 30° and 75° C. gave the following results:

Length parallel hex. axis

$$\begin{aligned} -\frac{\Delta l}{l_0} &= 12.98 \times 10^{-7}p - 5.32 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 13.55 \times 10^{-7}p - 7.82 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

Length perpendicular hex. axis

$$\begin{aligned} -\frac{\Delta l}{l_0} &= 1.946 \times 10^{-7}p - 1.11 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 2.025 \times 10^{-7}p - 1.47 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

From these we obtain for the cubic compressibility

$$\begin{aligned} -\frac{\Delta V}{V_0} &= 16.87 \times 10^{-7}p - 8.08 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 17.60 \times 10^{-7}p - 11.35 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

This value for the cubic compressibility is to be compared with that of Richards⁸ (17×10^{-7}), and of Adams, Williamson, and Johnston⁹

(17.1×10^{-7}), the latter value corrected using my recent value for the compressibility of iron. The agreement is to be considered rather good.

We have also to comment on the agreement between these results and the preliminary values which I have given in my paper on the compressibility of 30 metals. These preliminary measurements were only rough, and entirely satisfied their main purpose of bringing out the very great differences of linear compressibility in different directions. The specimens were not precisely oriented with respect to the crystal, so that it was not possible from the preliminary measurements to calculate the compressibility along the axes. However, since the measurements were made in three mutually perpendicular directions, the sum of the changes of length previously found should check with the change of volume given by the present measurements. The changes found were respectively 1.66×10^{-7} , 5.30, and 7.13. The sum of these is 14.90×10^{-7} , very appreciably less than the value found above. The explanation of the discrepancy I have found to be that the former specimen was not composed of a single grain, but was two, inclined at different angles. X-ray analysis had shown only one grain, but this analysis was made by the reflection method on one face, and was not able to show the second grain in the back part of the specimen. It is interesting that the lowest value found previously for the linear compressibility is less than the minimum for any direction in the single crystal; this is evidently a result of the constraint exerted on the one grain by the other.

The linear compressibilities give two relations between the five elastic constants. These follow in equations 1 and 2 in Abs. C. G. S. units. To obtain the other constants the following measurements were made. On one machined specimen 1.27 cm. in diameter the transverse expansion under a one-sided compression was measured, giving direct values for s_{13} and s_{12} . (Equations 3 and 4.) On another machined specimen, also 1.27 cm. in diameter, measurements were made of the longitudinal compression under a one-sided compressive stress and of the transverse expansion in two directions, giving direct values for s_{11} , s_{12} , and s_{13} (equations 5, 6, and 7). On so large a diameter as 1.27 cm. no appreciable effect from the machining is to be feared. Torsion measurements were made on 12 different rods, approximately 6 mm. in diameter, and inclined at various angles. These rods fall into three groups; in one group the hexagonal axis is nearly at 90° with the axis of the rod, in another the angle is nearly 50° , and in a third group, consisting of a single specimen, the angle is 7° . The vari-

ation of angle within the groups is so little that the average torsion coefficient within the group may be correlated with the average angle of inclination. These three groups, when averaged in this way, give three equations each containing the shearing constant s_{44} , equations 8, 9, and 10 respectively. In taking the averages, one result in the 50° group was discarded. In the 90° group the extreme range of the observed values was from 40 to 50, and in the 50° group from 62 to 69. Finally there are measurements of the change of length under tension of a number of rods 2.5 mm. in diameter inclined at various angles. Three of these are at angles so close to 90° that their results may be averaged, giving a direct value for s_{11} (equation 11). The extreme variation in this group is from 8.34 to 8.81. The other rods were inclined, one at 47° and the other at 66° (equations 12 and 13), and involve all the constants. It is to be remembered that one source of error with the unmachined rods is geometrical imperfections. The equations follow. The fundamental forms due to Voigt were used, and the special values of the direction cosines were substituted into them.

$$(1) \quad s_{11} + s_{12} + s_{13} = 1.932 \times 10^{-13},$$

$$(2) \quad 2s_{13} + s_{33} = 13.11 \times 10^{-13},$$

$$(3) \quad s_{13} = -6.64 \times 10^{-13},$$

$$(4) \quad s_{12} = +.31 \times 10^{-12},$$

$$(5) \quad s_{11} = 8.23 \times 10^{-12},$$

$$(6) \quad s_{13} = -6.74 \times 10^{-13},$$

$$(7) \quad s_{12} = +.48 \times 10^{-13},$$

$$(8) \quad s_{11} - s_{12} + \frac{1}{2}s_{44} = 23.1 \times 10^{-17},$$

$$(9) \quad 1.304s_{11} + .489s_{33} - .815s_{12} - .978s_{13} + .224s_{44} = 33.4 \times 10^{-13},$$

$$(10) \quad s_{44} = 26.0 \times 10^{-12},$$

$$(11) \quad s_{11} = 8.57 \times 10^{-13},$$

$$(12) \quad .535s_{11} + .217s_{33} + .249[2s_{13} + s_{44}] = 11.95 \times 10^{-13},$$

$$(13) \quad .697s_{11} + .027s_{33} + .138[2s_{13} + s_{44}] = 7.92 \times 10^{-13}.$$

The following are the final values adopted for the constants:

$$s_{11} = 8.23 \times 10^{-13},$$

$$s_{12} = +.34 \times 10^{-13},$$

$$s_{13} = -6.64 \times 10^{-13},$$

$$s_{33} = 26.38 \times 10^{-13},$$

$$s_{44} = 25.0 \times 10^{-13}.$$

As already mentioned, the linear compressibilities are much the most accurate. In choosing the best values for the constants, the first condition demanded was that the linear compressibilities should check exactly. In getting the rectangular constants by far the greatest weight was given to equations 3-7, as the specimens used there were much the best. In selecting the best value for s_{44} a more devious course of compromise was adopted, giving much weight to the direct value of equation 10. The success with which these values meet the required conditions can in many cases be told by inspection; the less obvious cases are equation 8, in which substitution of the values adopted gives 21.0 on the left hand side against 23.1 on the right, equation 9 with 30.4 against 33.4, equation 12 with 13.17 against 11.95, and equation 13 with 8.15 against 7.92.

The check afforded by this considerable number of independent measurements must, I think, be considered satisfactory, and gives considerable confidence in the final results. Particularly gratifying is the agreement between the cubic compressibility calculated from the linear compressibilities and that directly observed by other observers.

If now we compare these values with those of Grüneisen and Goens,² we note that their computed cubic compressibility is 19.0 against 17.1 experimental. Their s_{12} has the opposite sign from mine. The positive sign found here constitutes a distinct abnormality of zinc, but I believe that the experimental evidence for the positive sign is very strong (two direct measurements above). The values of Grüneisen and Goens were obtained from only two different sorts of measurements, extension and torsion measurements on rods of different orientations, and the elastic constants were computed so as to give as well as possible the observed variation with direction of the effective constants. It seems to me that the constants above, determined by more direct methods, are without doubt to be preferred.

The most striking feature of the elastic constants is the very great difference of the extensibility along and at right angles to the axis. The extensibility is greatest along the axis, which is what might be expected because the separation of the atoms is greatest in this direction.

Cadmium. The results which I have so far obtained on cadmium are incomplete and unsatisfactory in several particulars, and they must be considered as preliminary in character. There are two difficulties, neither of which I sufficiently realized until a large number of measurements had been made. In the first place the single crystal of cadmium is extraordinarily deformable, so that it is questionable whether it is allowable to attempt to machine it at all. My measurements of linear compressibility and thermal expansion were made on machined specimens, and these had to be entirely discarded. In the second place, under high pressures there are two new modifications, with reversible transitions. If pressure is applied to a single crystal of cadmium, it will be transformed into another crystal modification above a certain pressure, and then on still further increasing pressure into another. If now pressure is released into the domain of stability of the ordinary modification, it will not return in the original orientation. Hence all measurements of the properties under pressure of single cadmium crystals must be made on virgin pieces, which have never experienced either of the reversible transitions. The importance of this I did not realize for some time, and it explains a number of very puzzling and inconsistent results. The essentially new results which I have to communicate here are with respect to the transition.

Like zinc, cadmium is rather easy to crystallize, but is perhaps a little more exacting. I found more difficulty due to the formation of new nuclei. This difficulty I largely met by a more positive temperature control, lowering the glass mold into an oil bath, instead of into the air, which was adequate for zinc. The same speed of lowering as with zinc produced good results. It is also necessary that solid particles of dirt which may act as nuclei be more rigorously excluded. I succeeded, however, in growing crystals of the largest diameter, 2.2 cm. The purity of the cadmium is a matter of even greater importance than of zinc; the very deformable crystals are not obtainable unless the purity is high. I did not find any cadmium of American origin which was satisfactory, but used Kahlbaum's cadmium in all my final measurements.

The reflection pattern of cadmium is the same as that of zinc, but

with a stronger tendency to the development of the basal planes, and the nearly complete suppression of the other planes under some conditions. The pits, or negative crystals, of cadmium were larger than for any of the other metals, large enough so that the different individual faces could be readily studied under a magnification of 500.

Thermal Expansion. I obtained no results of value, the crystal structures of my specimens doubtless having been destroyed by the machining. However, the expansion has been measured by Grüneisen and Goens,² so that this lack is not of such importance. They find the same strikingly great relative expansion along the axis that is also shown by zinc.

Electrical Resistance. Measurements were made on a number of virgin pieces, and should therefore be satisfactory.

The specific resistances, obtained by the methods described, for a number of rods of Kahlbaum's cadmium, are shown in Figure 3 as a

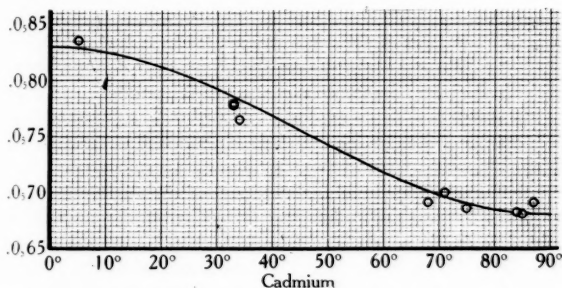


FIGURE 3. The specific resistance at 20° C. of cadmium as a function of the angle between the hexagonal axis and the direction of flow.

function of the orientation, together with the smooth curve of the theoretical resistances calculated according to Voigt's formula A. It appears that the best values for the specific resistances at 20° C. are 6.80×10^{-6} at right angles to the hexagonal axis, and 8.30 parallel to the axis. The ratio of these two resistances is 1.221. Grüneisen and Goens² find for the ratio 1.188. This is in closer agreement than our values for zinc, and the difference is in the opposite direction. However, their absolute values of specific resistance are much higher than mine, being (using their values for the temperature coefficient of resistance) 7.11×10^{-6} and 8.45 perpendicular and parallel respectively at 20° C. The difference is in the direction to be ac-

counted for by impurities in their sample, but the high value of their temperature coefficient would indicate high purity.

The specific resistance of the haphazard aggregate is 7.24×10^{-6} according to my measurements, and 7.51 according to Grüneisen and Goens. Jaeger and Diesselhorst¹⁰ have given 7.54 at 18° C. for cast cadmium.

I have no satisfactory measurements of the temperature coefficient of resistance, my observations having been made on specimens which had experienced a transition under pressure. One of these gave the high value 0.00428, so that it is probable that there is some direction in the crystal in which the coefficient is as high as this. This is higher than the value of Grüneisen and Goens above, 0.00426, which again is a little higher than the best previous value 0.00424 obtained in my pressure work on extruded wire, and also by Holborn.¹¹

The pressure coefficient was measured over the usual range of pressure, and at 0° and 95° C., but because of the polymorphic transitions produced by pressure, most of these readings are without significance for the effect of pressure on specimens of known orientation. However, it was fortunate that on the first application of pressure a seasoning application of 2000 kg. was made, releasing the pressure again to atmospheric after the application of 2000, so that the data are at hand by which the average pressure coefficient over the first 2000 may be found at 0° C. The results are as follows:

Angle of hexagonal axis with axis of specimen	Average pressure coefficient of measured resistance at 0° C. to 2000 kg/cm ² .
5°	-1.450×10^{-5}
87°	-0.693×10^{-5}

On the 5° specimen, readings were made at three intermediate pressures between 0 and 2000 and it was established that the effect is linear within the limits of error, but on the 87° specimen readings were made only at 0, 2000, and 0 again. The value of the coefficient which I have previously found for extruded cadmium wire was -1.063×10^{-5} . The results above on the single crystal give for the pressure coefficient of the haphazard aggregate, formula H of the introduction, -0.912×10^{-5} , less than the coefficient of the extruded wire. It is probable, therefore, that the orientation of the wire was not really haphazard, but that grains preponderated with the hexagonal axis parallel to the length of the wire.

Let us now consider what part of the difference of these coefficients

is to be ascribed to unequal changes of dimensions under pressure. Using the values of the elastic constants which will be presently given, the following approximate values are found:

$$5^{\circ} \qquad 87^{\circ}$$

Pressure coefficient of specific resistance -1.311×10^{-5} , -0.871×10^{-5} .

To a sufficient degree of approximation these may also be taken as the coefficients of specific resistance respectively parallel and perpendicular to the hexagonal axis.

The effect of the change from measured to specific resistance is the same that it was with zinc, namely the coefficients in the two directions become more nearly equal, but as before, there is left a comparatively large outstanding difference, the specific resistance in the direction of the hexagonal axis (which is also the direction of greatest resistance) being decreased more rapidly than the resistance at right angles.

Elastic Constants. It has already been explained that many of the measurements of the elastic constants were vitiated either because the stresses producing the deformation to be measured exceeded the elastic limit, or else because the crystal structure had been destroyed by machining or by subjection to pressure with polymorphic transition. The measurements on compressibility had to be discarded entirely, the linear compressibilities failing entirely to check with known values of the cubic compressibility. This was true even for the initial compressibilities found before the polymorphic transition had been produced, and the only explanation seems to be a destruction of the crystal structure by machining. Among the other measurements of the constants were also some which were evidently impossible. It was possible, however, to select from the fifteen measurements enough to give fair values for the constants. In selecting the measurements to use I was guided by Grüneisen and Goens. This, however, was merely by way of saving time, because the inconsistent measurements discarded were inconsistent by large amounts, and were very different from those accepted.

The following sorts of measurements were used in obtaining the final results. The extension under tension of two rods nearly parallel and perpendicular respectively to the hexagonal axis gave direct values of s_{11} and s_{33} . The torsion was measured of a rod at 90° (average of two specimens), and the tension and torsion of a rod at 30° . There were thus five measurements available for the five constants, for which I have adopted the following values as best:

$$s_{11} = 12.9 \times 10^{-13},$$

$$s_{12} = -1.5 \times 10^{-13},$$

$$s_{13} = -9.3 \times 10^{-13},$$

$$s_{33} = 36.9 \times 10^{-13},$$

$$s_{44} = 64.0 \times 10^{-13}.$$

In addition to my five measurements there is the condition imposed by the cubic compressibility of other observers. I chose the constants so as to check almost exactly with the cubic compressibility of Adams, Williamson and Johnston⁹ (22.5×10^{-13} against 22.4), and also used the directly measured values of s_{11} and s_{33} . The other constants were chosen so as to give as good a compromise as possible when substituted in the three remaining equations. In these equations the agreement was as follows: 46.4 against 43.5, 28.6 against 29.8, and 64.1 against 65.0. The agreement is not bad, but it must nevertheless be recognized that these constants are not nearly as secure as those of zinc, or for that matter most of the other metals measured here.

Compared with the values of Grüneisen and Goens, the most important difference is in the larger value which I find for s_{44} , 64 against 54. It is to be noticed that I have given negative values to both s_{12} and s_{13} , unlike zinc. In doing this I was doubtless influenced by the values of Grüneisen and Goens; I do not believe that this result should be accepted as final or made the basis of theoretical considerations without further verification, preferably a direct measurement, such as was possible for zinc.

Transitions of Cadmium under Pressure. These results are preliminary, and have to do chiefly with proving the existence of the transitions, and establishing their approximate locations. Most of the results were obtained in the course of attempts to measure the linear compressibility. These measurements were made first on specimens cut at right angles to the axis, and the first suggestion of anything wrong was in the unusually large permanent changes of zero after an excursion to the maximum pressure and back again. The curve itself was fairly regular, but careful study showed irregularities greater than could be explained by experimental error. Measurements were now made on the specimen parallel to the axis, and the effects found were much greater. At two places on the curve there were discontinuities by amounts rising in the extreme case to as

much as 2% of the total change of length under 12000 kg. These discontinuities were reversible in the sense that they could be obtained in approximately the same location with increasing or decreasing pressure, but there were peculiarities which made them unlike the volume discontinuities ordinarily found in measuring transitions. It must be remembered that these were discontinuities of length. The discontinuities were not always of the same sign, but the change of length might be either a decrease or an increase.

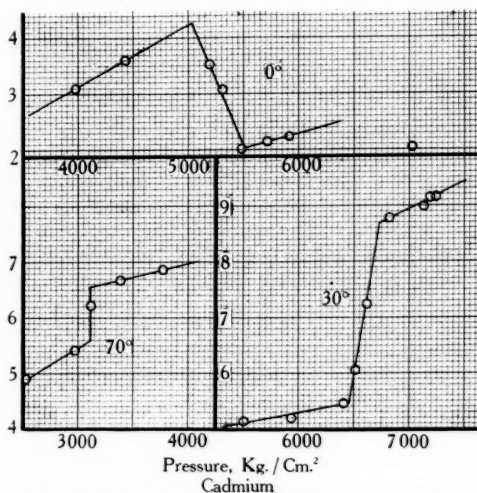


FIGURE 4. Shows the discontinuity of length on an arbitrary scale observed at the transition points of cadmium under pressure. For the high pressure transition an example is shown of both an increase and a decrease of length.

Furthermore, after several changes of pressure back and forth, the discontinuity usually became less and less pronounced and ultimately practically disappeared. In one case, after several applications of pressure, the discontinuity, which at first was an increase, reversed and became a decrease of length. The most valuable measurements were always obtained on virgin specimens. In Figure 4 are shown the best examples of the two discontinuities; at the higher pressure an example is shown of both an increase and a decrease of length. In some cases it was possible to obtain readings within the

discontinuity itself, as shown in the figure, and in others it was only possible to shut the discontinuity within limits.

Having established the existence of the effect by compressibility measurements, I verified its existence by finding a discontinuity in the electrical resistance of a rod whose hexagonal axis was parallel to the length, which is the most favorable orientation.

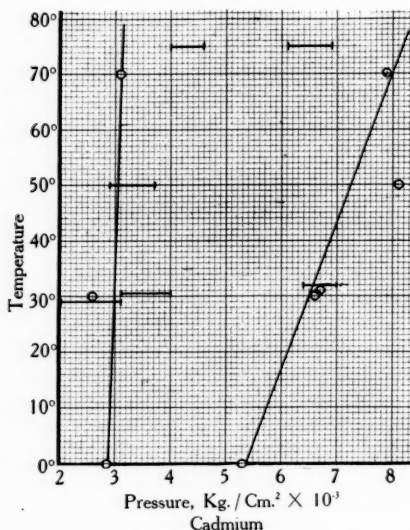


FIGURE 5. The observed transition pressures of cadmium as a function of temperature. The circles indicate readings obtained within the discontinuity, the two phases being simultaneously present, while the lines show the range within which the transition was shut by other readings obtained with only one phase present and therefore not under equilibrium conditions.

The collected results are shown in Figure 5, where the points indicate the readings determined within the actual discontinuity, and the lines indicate the range within which the transition was included when it was not more exactly located. The existence of the transition must be considered to be beyond doubt, and also the location approximately as given, but the reason for the discrepancies between readings obtained at different times is not altogether clear. It is possible that it may be an effect of internal stress. If the new modification does not appear as a single crystal, but as several grains of different

orientations, there may well be a stress due to the unequal change of dimensions, which may modify the transition pressure. It is well known that the effects of a non-hydrostatic stress on a transition point may in some cases be very large, particularly when the heat of transition is low.

Whatever the other properties of the new modifications, it is evident that they cannot differ appreciably in volume from the ordinary modification, but that the spacing of the atoms in different directions must differ, being in some directions extended and in others contracted. This is demanded not only by the facts found here, but also by the fact that I have never before found any suggestion of such a discontinuity. I have previously measured the pressure coefficient of resistance, the compressibility, and the thermal e.m.f. under pressure, but always on specimens of many grains arranged approximately at haphazard. It follows that the electrical properties also of the new modifications can, on the average, differ only slightly from the ordinary.

One is at once reminded of the polymorphic transitions claimed by Cohen¹² for cadmium, but it is probable that there is no connection, the transitions found here being reversible, and occurring only at pressures of several thousand kilograms.

Bismuth. The source of most of the lead used in these measurements was the U. S. S. Lead Refining Co., to whose courtesy I owe some especially refined electrolytic bismuth. Some of this material has been used in my previous work,¹³ and some of the identical lot was left for my present work; I also procured a fresh lot made by the same method. In my previous work will be found a chemical analysis; the chief impurity is less than 0.03% Ag. The purity is also vouched for by the high value of the temperature coefficient of resistance. Furthermore, it is to be remembered that the process of crystallization acts as a very efficient purification, at least from those metals which depress the freezing point. I have found that the lower end of a casting of commercial bismuth yields metal of as high a temperature coefficient as the best electrolytic material.

Bismuth is one of the most strongly crystalline of metals, and until the recent work of Grüneisen and Goens is practically the only metal for which any attempt has been made to obtain data for the individual crystal. The previous material has been usually obtained from large single crystals found in the interior of large masses of slowly solidified bismuth. There have, however, probably been large errors introduced by the methods of manipulation, as will be explained later. It was a

surprise, in view of this previous experience with bismuth, to find that it is not one of the easiest to grow in large single crystals. My usual method of growth readily produces rods which to the first casual inspection are one grain, either by the reflection or the cleavage test, but on closer examination it will be found that what appears as a single cleavage plane is really not one but several inclined at very slight angles to each other. Instead of a single grain, it is therefore much more usual for the casting to consist of several, all oriented very nearly alike, and growing together for the entire length of the casting. Not only is the orientation of the cleavage plane, and therefore of the trigonal axis, nearly the same in these different grains, but the orientation of the other axes about the axis of three-fold symmetry is also approximately the same, because the cleavage on the rhombohedral planes, which is well developed in bismuth although not nearly as perfect as that on the basal plane, runs across from one grain to another with very slight change of direction. I did not succeed in obtaining any of the largest castings (2.2 cm. diameter) in one grain, and only one as large as 1.2 cm. The smaller castings, 2 to 6 mm. in diameter, came much more readily in one grain. The presence of several grains has no effect on the determination of certain properties, such as the linear compressibility under hydrostatic pressure, but it may introduce rather large errors into the determination of certain other combinations of the elastic constants, such for instance as depend on the deformation under a one-sided compression. Considerable trouble from this cause was experienced before the reason was located. Toward the end of my manipulations of bismuth I found that the best results are obtained with a high rate of cooling, instead of a low rate as for zinc and cadmium, and I have no doubt that with a little pains it would now be possible to obtain the larger castings.

The preferred manner of growth, as also for zinc and cadmium, is with the basal plane parallel to the axis of the casting, but variations from this direction take place more readily than they do for zinc. In the small sizes it is possible to obtain large departures from parallelism, but because of the extreme ease of cleavage along the basal plane, I did not find it feasible to attempt measurements on any long slender rods with an angle of inclination greater than 45° , although measurements were made on machined pieces short compared with their length in which the basal plane was at right angles to the length.

A particular source of trouble with bismuth was the great amount of occluded gas set free on solidifying, which makes special trouble with the long slender castings. The gas must be removed by a prolonged preliminary heating in vacuum, as already explained.

Thermal Expansion. This was measured in the regular way on the same two specimens whose linear compressibility was determined. The specimens were machined from a large casting, were 6 mm. in diameter, and 2.8 cm. long perpendicular to the trigonal axis, and 2.1 cm. parallel, this latter being in two pieces. The following results were found at 20° C.:

$$\alpha_1 = 10.36 \times 10^{-6},$$

$$\alpha_{11} = 13.96 \times 10^{-6}.$$

The expansion is thus greatest along the axis of rotational symmetry, as it has always been found to be, but the difference is very much less accentuated than it is for zinc and cadmium. This is perhaps surprising when the strongly crystalline character of bismuth is considered.

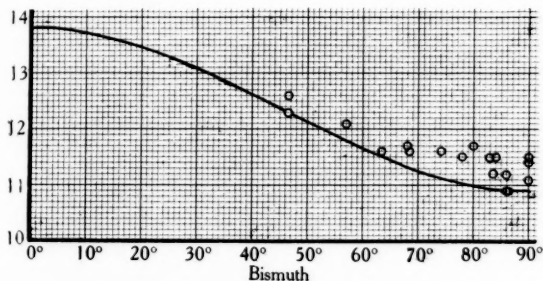


FIGURE 6. The specific resistance at 20° C. multiplied by 10^5 of bismuth as a function of the angle between the trigonal axis and the direction of flow.

The thermal expansion at 40° C. has been found by Fizeau to be 16.2 parallel and 12.1×10^{-6} perpendicular to the axis, both greater than the values above. The reason for the discrepancy is not clear, unless there were flaws in Fizeau's specimen, which seems to have been the case with many of the early specimens because of their method of preparation.

Electrical Resistance. Measurements were made on the specific resistance at room temperature of about 20 specimens, all unmachined rods, inclined at various angles up to 45°. These are shown in Figure 6 (two have been discarded, lying impossibly high), and I have also drawn the curve which seems to represent the most probable

value of the true resistance. The points scatter a great deal, and lie above the curve. The reason for this is to be sought perhaps partly in fissures introduced into the bismuth by handling, the cleavage being very easy, and also by geometrical imperfections, especially minute bubbles on the sides of the casting, which I have never succeeded in completely eliminating.

The most probable values of the specific resistance at 20° C. may be deduced from the diagram to be

$$\rho_L = 109 \times 10^{-6},$$

$$\rho_{11} = 138 \times 10^{-6}.$$

The ratio of the resistances in the two principal directions is thus 1.27.

These results differ considerably from those of previous observers. Thus Matteucci¹⁴ finds for the ratio of the two principal resistances 1.6, Borelius and Lindh¹⁵ 1.57, and van Everdingen¹⁶ 1.68. The difference is in the direction to be expected. It has been brought out by Borelius that most resistance measurements have been faulty because of the existence of flaws in the metal. Their existence may be shown very strikingly by subjecting the metal to a compression at right angles to the basal plane, when the resistance experiences a sudden and large decrease. The effect is so large that Borelius has even gone so far as to suggest that if there were no fissures the resistance would be the same in all directions. These fissures are an almost certain result of the method of preparation which many previous experimenters have adopted. Thus Borelius describes slowly cooling a dish of bismuth 3 cm. high and 2 cm. in diameter with every precaution to ensure the slow growth of the crystal, then breaking the casting in two, judging from the continuity of the cleavage plane that there was really only one grain, and then using the two halves of the broken casting as the source of further material. Such treatment would be expected to produce fissures on the basal plane, and to give exactly the larger value for the resistance along the axis (across the planes) which was actually found. That my values above do not suffer from this source of error is made probable by the extreme care with which the glass tubes were broken from the castings, and more especially by the measurements of the pressure coefficient of resistance. If there are minute fissures, these will be closed by a small initial pressure, so that there will be an initial sharp decrease of resistance at a different rate from the subsequent rate. No such effect was found.

Whatever the uncertainties shown in Figure 6, it is evident that the ratio of the resistances in the two directions must be much less than 1.6. The highest ratio which seems at all consistent with the data is 1.31.

From the results above it may be calculated that the resistance of a haphazard collection of grains in all orientations is 117×10^{-6} , which agrees closely with the value 119 at 18° C. found by Jaeger and Diesselhorst,¹⁰ and is confirmatory evidence of the correctness of the small ratio of the principal resistances found above.

Temperature Coefficient of Resistance. This was determined for two samples incidentally during the measurements of pressure coefficient of resistance, the angle of inclination of the axis to the length of these two pieces being respectively 90° and 57°. The measurements on the 90° sample were a little more regular, and gave the following results for the resistance as a function of temperature:

Temperature	Relative Resistance
0°	1.000
25	1.102
50	1.209
75	1.322
100	1.444

The departure from linearity is in the normal direction. Within the limits of error, which were not more than 1% on the coefficient, the measurements on the 57° sample agreed with the above, so that there appears to be no appreciable variation of temperature coefficient with direction. Corrected for thermal expansion, the mean coefficient between 0° and 100° C. of specific resistance is 0.00445, the same in all directions.

The average coefficient of the measured resistance given by the above is 0.00444, which is a trifle higher than the best value which I have previously found for electrolytic bismuth (0.00441) and is evidence of high purity. Holborn,¹¹ however, has found a value 0.00446.

Pressure Coefficient of Resistance. The effect of pressure to 12000 kg. at several temperatures was measured on the two samples described above in connection with the temperature coefficient. The results are not linear with the pressure, and are not conveniently given by formulas, so I have reproduced them in a Table I. There was no especial incident in making the measurements; the regularity was that to be expected from a specimen of small resistance. With

the 90° specimen the average deviation from a smooth curve varied with the temperature from 1.1 to 0.6% of the effect, and with the 57° specimen the variation was from 0.06 to 0.5%.

TABLE I.
RELATIVE RESISTANCES OF BISMUTH UNDER PRESSURE,

Trigonal axis perpendicular to length				
Pressure kg/cm ²	Relative Resistance			
	0° C.	30° C.	62° C.	95° C.
0	1.0000	1.0000	1.0000	1.0090
1000	1.0090	1.0092	1.0082	1.0005
2000	1.0188	1.0187	1.0188	1.0199
3000	1.0294	1.0289	1.0292	1.0305
4000	1.0404	1.0395	1.0403	1.0416
5000	1.0518	1.0511	1.0518	1.0534
6000	1.0637	1.0627	1.0635	1.0656
7000	1.0758	1.0750	1.0758	1.0782
8000	1.0884	1.0876	1.0885	1.0914
9000	1.1010	1.1003	1.1013	1.1046
10000	1.1143	1.1133	1.1144	1.1182
11000	1.1279	1.1263	1.1276	1.1320
12000	1.1418	1.1393	1.1409	1.1463
Trigonal axis 57° to length				
Pressure kg/cm ²	Relative Resistance			
	0° C.	30° C.	95° C.	
0	1.0000	1.0000	1.0000	
1000	1.0155	1.0149	1.0126	
2000	1.0319	1.0305	1.0270	
3000	1.0490	1.0475	1.0423	
4000	1.0671	1.0648	1.0574	
5000	1.0873	1.0831	1.0755	
6000	1.1065	1.1024	1.0929	
7000	1.1278	1.1218	1.1110	
8000	1.1501	1.1422	1.1300	
9000	1.1733	1.1637	1.1499	
10000	1.1971	1.1854	1.1706	
11000	1.2213	1.2081	1.1917	
12000	1.2471	1.2318	1.2129	

As has already been found for extruded wire, the effect of pressure is to increase the resistance, the rate of increase itself becoming

greater at the higher pressures. We now find that the increase under pressure is more rapid across the cleavage planes than at right angles. This is the reverse of the effect to be expected if the cleavage planes are the seat of incipient fissures.

We have now to compute from the effects at 90° and 57° the effect at 0° (cleavage plane perpendicular to the length). In making this computation we have first to calculate the pressure coefficients of specific resistance at 90° and 57° . The formulas already given, together with the elastic constants to be given in the next section, give for the correction term -1.6×10^{-6} at 90° and -1.16×10^{-6} at 57° , of which latter -0.11×10^{-6} is the angle correction. The data given above for resistance as a function of pressure yield for the initial pressure coefficients of measured resistance 9.1×10^{-6} and 14.6×10^{-6} at 90° and 57° respectively. Applying the corrections, we get for the pressure coefficients of specific resistance $+7.5 \times 10^{-6}$ and $+13.4 \times 10^{-6}$ at 90° and 57° . Substituting now these values in formula C for the pressure coefficient of specific resistance as a function of direction, we obtain for the pressure coefficient of specific resistance along the axis $+24.5 \times 10^{-6}$, which is thus three times larger than the coefficient in the perpendicular direction.

Elastic Constants. Bismuth is characterized by six elastic constants; five of these enter in the same way as the five constants of zinc and cadmium and may be determined in the same way, the sixth is the so-called cross constant s_{14} and requires different sorts of measurement. In getting these constants a number of measurements had to be discarded, because it was found that the specimens were not a single grain, but several of almost exactly the same orientation. Some of the constants determined with these multigrained rods were of the order of twice the correct values.

The measurements from which the constants were finally deduced were as follows. First and most accurate, the linear compressibility of specimens parallel and perpendicular to the trigonal axis, giving equations 1 and 2. Only the initial values of the compressibilities from these pressure measurements are to be used in combination with the other elastic constants; the behavior of the linear compressibility over the pressure range will be described later. Second, direct measurements of the longitudinal compression and two transverse expansions of a machined specimen 1.27 cm. in diameter perpendicular to the trigonal axis subjected to a simple compressive stress, giving equations 3, 4, and 5. These measurements give direct values for s_{11} , s_{12} , and s_{13} . Thirdly, measurements were made of the

torsion of two rods with the cleavage plane parallel to the length, giving by the average equation 6. The two constants for the two rods differed by 1.7%. Finally to determine s_{14} , measurements were made of the extension under tension of three rods inclined at various angles from 46.5° to 74° , giving equations 7, 8, and 9. In making these determinations it is necessary to know the location of the rhombohedral cleavage planes as well as the basal cleavage plane. Each of these tension measurements gave a value for s_{14} , using in the equation the values for the other constants which seemed best from the previous equations. Each of the values of s_{14} is the difference of two quantities of nearly the same magnitude, so that it is not to be expected that the result will have any great accuracy. The three values so obtained were averaged to obtain the final value, weighting the different values according to the ratio of the difference to the larger of the two terms of the equation.

The equations in detail are as follows:

- (1) $s_{11} + s_{12} + s_{13} = 6.66 \times 10^{-12},$
- (2) $2s_{13} + s_{33} = 16.28 \times 10^{-12},$
- (3) $s_{12} = -13.8 \times 10^{-13},$
- (4) $s_{13} = -6.1 \times 10^{-13},$
- (5) $s_{11} = 27.3 \times 10^{-13},$
- (6) $s_{11} - s_{12} + \frac{1}{2}s_{44} = 95.3 \times 10^{-13},$
- (7) $s_{14} = (60.4 - 44.2) \times 10^{-13} = 16.2 \times 10^{-13},$
- (8) $s_{14} = (53.7 - 36.0) \times 10^{-13} = 17.7 \times 10^{-13},$
- (9) $s_{14} = (90.8 - 80.0) \times 10^{-13} = 10.8 \times 10^{-13}.$

Equations 1 and 2 for the linear compressibility may be checked against the cubic compressibility. The value found by adding 2 to twice 1 is 29.60×10^{-13} for the cubic compressibility; the experimental values are $29.7(5)$ by Adams, Williamson, and Johnston,⁹ and 29×10^{-13} by Richards.⁸ The agreement is probably within the limits of error. The first two equations were therefore accepted as correct. The rectangular constants were now chosen approximately, as given by equations 3 to 5, but with slight readjustments in s_{11} , s_{12} , and s_{13} so as to satisfy equation 1. s_{33} is then given immediately by equation 2, but there is no check on it. The magnitude

of the adjustments of the first three constants gives an idea of the probable accuracy. The shearing constant s_{44} was then obtained directly from 6 by substitution. In equations 7 to 9 the values of the first five constants thus found were substituted, giving the equations as they stand for s_{14} . The weighting process described gave the final value for s_{14} . The final values for the constants follow in Abs. C.G.S. units.

$$s_{11} = 26.9 \times 10^{-13},$$

$$s_{12} = -14.0 \times 10^{-12},$$

$$s_{13} = -6.2 \times 10^{-12},$$

$$s_{33} = 28.7 \times 10^{-12},$$

$$s_{44} = 104.8 \times 10^{-13},$$

$$s_{14} = 16.0 \times 10^{-13}.$$

In contrast with zinc and cadmium, the two constants s_{11} and s_{33} have nearly the same values. The exceedingly large value of the shearing constant s_{44} is the particularly interesting feature for bismuth.

So far as I know there are no previous values for the individual elastic constants of bismuth. This is surprising in view of the fact that others of its physical constants have been determined, and that large crystals are obtained so readily. It is probable that minute fissures lead to larger inconsistencies in the elastic constants than in some of the others; witness the discrepancies found above when there were several grains.

Finally we have the linear compressibility as a function of pressure. These measurements ran as smoothly as any of the linear compressibility measurements, and gave the following results, pressure in kg/cm²:

Length perpendicular to hexagonal axis

$$\begin{aligned} -\frac{\Delta l}{l} &= 6.624 \times 10^{-7}p - 4.39 \times 10^{-12}p^2, & \text{at } 30^\circ, \\ &= 7.044 \times 10^{-7}p - 8.40 \times 10^{-12}p^2, & \text{at } 75^\circ. \end{aligned}$$

Length parallel to hexagonal axis

$$\begin{aligned} -\frac{\Delta l}{l} &= 15.92 \times 10^{-7}p - 11.1 \times 10^{-12}p^2, & \text{at } 30^\circ, \\ &= 15.80 \times 10^{-7}p - 11.6 \times 10^{-12}p^2, & \text{at } 75^\circ. \end{aligned}$$

These measurements were on electrolytic bismuth of high purity. Measurements were also made on a specimen of commercial bismuth perpendicular to the axis, giving

$$\begin{aligned} -\frac{\Delta l}{l} &= 6.450 \times 10^{-7}p - 4.60 \times 10^{-12}p^2, & \text{at } 30^\circ, \\ &= 6.423 \times 10^{-7}p - 4.57 \times 10^{-12}p^2, & \text{at } 75^\circ. \end{aligned}$$

The difference, due to impurity, is about 2.7%.

Combining the above results for the change of length gives for the change of volume of electrolytic bismuth:

$$\begin{aligned} -\frac{\Delta V}{V_0} &= 29.17 \times 10^{-7}p - 22.43 \times 10^{-12}p^2, & \text{at } 30^\circ, \\ &= 29.89 \times 10^{-7}p - 31.13 \times 10^{-12}p^2, & \text{at } 75^\circ. \end{aligned}$$

Antimony. It is astonishingly easy to obtain antimony in single grain castings; it does not have the tendency to form several grains of nearly the same orientation that bismuth does. Because of the high melting point, it is necessary to use a mold of quartz or of high melting combustion tubing; pyrex softens below the melting point. When using combustion tubing, care is necessary not to exceed the melting point too much; I obtained good results by running the furnace 50° above the melting point. I used the slowest rate of cooling, 4 mm. an hour for the largest size casting, but I have no doubt that considerably more rapid rates would be equally satisfactory. Remarkably clean castings were obtained, with practically none of the trouble from occluded gas shown by bismuth. The preferred manner of growth is with the trigonal axis perpendicular to the axis of the casting, that is, with the principal cleavage plane parallel to the length. The larger castings, 2.2 cm. down to 6 mm., invariably came out with this orientation, but the smaller castings of 2 mm. diameter gave a number of oblique incidences up to 65° .

Thermal Expansion. The regular apparatus and procedure were used. The specimens were cut from one of the large castings, and were the same as those used for the linear compressibility. There is no difficulty in preparing the specimen with the cleavage plane parallel to the length, but because of the excessively easy cleavage there was considerable difficulty in preparing the perpendicular specimen. This specimen was built up of three short pieces resting against each other on natural cleavage faces, which are as flat and parallel as it would be possible to obtain by a machining operation. These short

pieces, approximately cubical, were cut from a slab of the requisite thickness by grinding with a thin slitting wheel. A special brass clamp was made with which the specimens were firmly compressed across the cleavage planes, and in addition they were imbedded in a matrix of cement. In cutting, the clamp and the specimens were ground across together; this proved to be necessary because the specimen must be always firmly clamped on both sides of the cut.

The readings with the specimens so prepared were as self consistent as those obtained with less cleavable metals. The following results were found for the expansion in a range of 10° about room temperature:

$$\alpha_{11} = 15.56 \times 10^{-6},$$

$$\alpha_1 = 7.96 \times 10^{-6}.$$

The expansion across the cleavage planes is thus nearly twice as great as that at right angles; this is the normal type of behavior, and is that found for all the metals examined here.

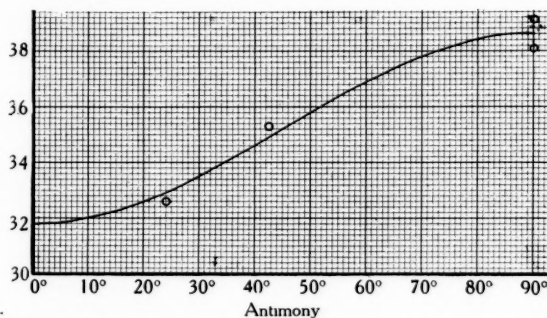


FIGURE 7. The specific resistance of 0° C. multiplied by 10^4 of antimony as a function of the angle between the trigonal axis and the direction of flow.

At 40° C. Fizeau has found for the expansions 16.92 and 8.82×10^{-6} respectively, both larger than my corresponding values. The difference is in the same direction as for bismuth. At least part of the difference is to be ascribed to the difference of temperature.

Resistance. The specific resistance of four small castings was measured; at angles varying from 24° to 90° . The specific resistances at 0° C. as a function of orientation, and the most probable curve, are shown in Figure 7. The specific resistance parallel to the axis

(across the cleavage planes) is 31.8 and at right angles 38.6×10^{-6} . This is the first time that we have found a resistance across the cleavage plane less than in the perpendicular direction, and is not what we might expect. It is evident that this sort of result cannot be explained by the presence of minute fissures.

There are no previous determinations for comparison. We may obtain a sort of check by computing the resistance to be expected in an aggregate of crystals of haphazard orientation. This turns out to be 33.8×10^{-6} at 0° C. This may be compared with 38.7 at 0° given in Bureau of Standards Circular No. 74, 1918. The difference may be ascribed to differences of purity, the Bureau having used American antimony, which is always less pure, judging by the melting point, and may also be in part due to the microscopic fissures which would be expected in a haphazard casting because of the unequal thermal expansions in different directions of the different grains.

The temperature coefficient of resistance of three of the above four samples was determined between 0° and 95° ; the specimen at 24° to the axis was damaged by an application of pressure before the temperature coefficient could be determined. These temperature determinations were made with especial care, the temperature being run through a complete cycle, from 0° to 95° back to 0° with intermediate readings, and in one case back to 95° again. In all cases the readings were all that could be asked, there was no hysteresis and no permanent change, but the readings were in all cases single valued functions of the temperature within the sensitiveness of the readings. The two specimens perpendicular to the axis gave results indistinguishable from each other. The following values were found for the resistance as a function of temperature.

Temp. °C.	Length 90° to axis	Length 42.5° to axis
0	1.000	1.000
25	1.120	1.126
50	1.245	1.260
75	1.375	1.401
100	1.510	1.550

There is thus a very perceptible difference between the temperature coefficients in different directions.

We may now calculate the temperature coefficient across the cleavage planes. We first find the temperature coefficient of specific resistance to be 0.00511 for the 90° direction and 0.00552 for the 42.5°

direction. Substituting these values and the resistances in formula C yields 0.00595 for the 0° direction for the specific resistance. The variation with direction is the largest yet found.

The temperature coefficient of the haphazard aggregate may be calculated from these results to be 0.00510.

Resistance of Antimony under Pressure. It is already known that antimony in the haphazard aggregate is unusual in that the resistance increases under pressure. The behavior is that normal to this type of conductors in that the rate of increase under pressure itself increases as the pressure increases. The measurements on single crystals have now disclosed further abnormalities, which make antimony unique. These new abnormalities are associated with conduction perpendicular to the trigonal axis; parallel the behavior is more normal. Perpendicular to the axis at 0° C. the resistance increases under pressure, as it does in the haphazard aggregate, and at first the rate of increase increases with rising pressure, but presently there is a point of inflection near 6000 kg., and above this pressure the rate of increase decreases with rising pressure. At 95° C. on the other hand, the resistance decreases under pressure, which is the normal behavior for most metals, but the curvature is anomalous; at low pressures the rate of decrease itself decreases with rising pressure, but there is a point of inflection, and above this the rate increases. At the intermediate temperature at 50° C. the behavior is a compromise between that at 0° and 95° ; at low pressures the resistance increases, but passes through a maximum and from here on decreases. This is the first example of a maximum resistance as far as I know; it is to be set by the side of the minimum resistance which I have recently found for caesium.

This unusual behavior was verified on two samples. On the repetition, more care was taken in the preparation of the sample, especially in being sure that the current leads made soldered connections across the entire section of the specimen, so that any fissures developed between the cleavage planes would not have the effect of insulating part of the sample from the rest and so changing the resistance. The results found with the two samples agreed at the maximum pressure within 0.2% of the total resistance at 0° C., and 0.5% at 95° .

Measurements on the sample with the axis at 42.5° to the length gave normal results in that the resistance increases under pressure at all temperatures, and the curvature is normal, the rate of increase of resistance under pressure also increasing with pressure, but the temperature effect is unusual in that the rate of increase at the higher

temperatures is relatively and absolutely less than at the lower temperatures. I made a further attempt at resistance measurements on

TABLE II
RESISTANCE OF ANTIMONY UNDER PRESSURE.

Trigonal axis 90° to length			
Pressure kg/cm ²	Resistance		
	0° C.	50° C.	95° C.
0	1.0000	1.2450	1.4830
1000	1.0035	1.2460	1.4808
2000	1.0085	1.2481	1.4787
3000	1.0140	1.2506	1.4765
4000	1.0204	1.2533	1.4744
5000	1.0275	1.2561	1.4722
6000	1.0347	1.2587	1.4702
7000	1.0416	1.2610	1.4674
8000	1.0479	1.2628	1.4645
9000	1.0532	1.2640	1.4610
10000	1.0580	1.2646	1.4575
11000	1.0622	1.2645	1.4530
12000	1.0650	1.2632	1.4475

Trigonal axis 42°.5 to length			
Pressure kg/cm ²	Resistance		
	0° C.	50° C.	95° C.
0	.9040	1.1391	1.3732
1000	.9136	1.1476	1.3825
2000	.9242	1.1571	1.3904
3000	.9351	1.1674	1.3992
4000	.9473	1.1782	1.4089
5000	.9607	1.1903	1.4195
6000	.9760	1.2030	1.4298
7000	.9913	1.2161	1.4411
8000	1.0064	1.2302	1.4523
9000	1.0218	1.2435	1.4638
10000	1.0370	1.2567	1.4755
11000	1.0523	1.2700	1.4872
12000	1.0676	1.2834	1.4987

a sample with the cleavage planes inclined at 66° to the length, but these were not successful, there being very large permanent changes of resistance after every application of pressure. This is doubtless

due to the opening of fissures between the cleavage planes, for which the viscosity of the transmitting medium must have been responsible.

The results obtained with the 90° and the 42.5° specimens are shown in Table II and Figure 8. These give the measured resistance

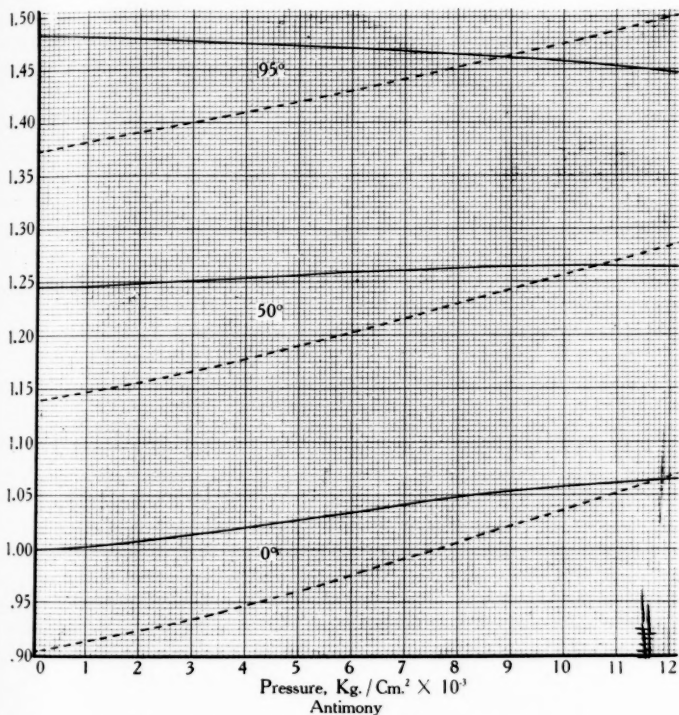


FIGURE 8. The relative resistances at 0° , 50° , and 95° C. of antimony as a function of pressure in two different directions in the crystal. The full lines show the resistance 90° to the trigonal axis, and the dotted lines 42.5° to the axis.

at intervals of 1000 kg. at 0° , 50° , and 95° C. in terms of the resistance at 0° C. for the 90° direction as unity. The figure brings out the very interesting result that the abnormalities under pressure are connected with the abnormal result found at atmospheric pressure that the

resistance across the cleavage planes is less than that at right angles. At high pressures, this behavior is reversed, and the resistance across the cleavage planes becomes greater, as we have found it for all the other metals. In this respect the effect of pressure is to compel a return to the normal type of behavior. Furthermore, the return to normal appears to be more rapid at the higher temperatures, and is connected with the unusual temperature effects.

We may now obtain from the coefficients of measured resistance approximate values for the coefficients of specific resistance, using for the elastic constants at all temperatures the values found at room temperature (the error so introduced must be small). We find in the first place that the initial pressure coefficient for the 90° direction of the axis is $+10.5 \times 10^{-7}$ at 0° C. and -1.7×10^{-7} at 95° C. For the 42.5° direction, the initial pressure coefficients of specific resistance are respectively $+90.4 \times 10^{-7}$ and $+66.4 \times 10^{-7}$. Using now formula C, we find for the 0° direction of the axis that the initial pressure coefficient of specific resistance at 0° C. is 172×10^{-7} and 131×10^{-7} at 95° C. These are of the same order of magnitude, but less, than found for bismuth.

Elastic Constants. The rectangular constants were obtained in the first place by measurements of the linear compressibility parallel and at right angles to the trigonal axis, equations 1 and 2. The specimens used for these measurements have already been described in connection with the thermal expansion measurements. Secondly, measurements were made of the longitudinal compression and two transverse expansions under one-sided compression of an unmachined casting with cleavage planes parallel to the length, giving direct values for s_{11} , s_{12} , and s_{13} , in equations 3, 4, and 5. Thirdly, a measurement of the extension under tension of a natural casting with the cleavage plane parallel to the length gives another independent direct value for s_{11} , equation 6. The shearing constant s_{44} was determined by a torsion measurement on a single specimen with cleavage plane parallel to the length, equation 7. The cross constant s_{14} I attempted to get from measurements of the extensions under tension of two inclined rods, but one of these had to be discarded, the casting being curved, and so receiving additional curvature under tension. The data retained for s_{14} are in equation 8. The equations follow:

- | | |
|-----|--|
| (1) | $s_{11} + s_{12} + s_{13} = 5.40 \times 10^{-12},$ |
| (2) | $2s_{13} + s_{33} = 16.84 \times 10^{-12},$ |
| (3) | $s_{13} = -9.3 \times 10^{-13},$ |

- (4) $s_{11} = 17.6 \times 10^{-13}$,
 (5) $s_{12} = -4.2 \times 10^{-13}$,
 (6) $s_{11} = 17.8 \times 10^{-13}$,
 (7) $2(s_{11} - s_{12}) + s_{44} = 84.0 \times 10^{-13}$,
 (8) $.908s_{11} + .002s_{33} + .0445(2s_{13} + s_{44}) -$
 $0.396s_{14} = 20.3 \times 10^{-13}$.

We have thus 8 equations for the 6 constants. An additional check is given by the cubic compressibility to be calculated from equations 1 and 2. This is found to be 27.64×10^{-13} against 24 (given to only two significant figures) by Richards.⁸ The agreement is probably within experimental error, and I have accepted equations 1 and 2 as correct. Equations 4 and 6 give two direct values of s_{11} differing by about 1%. I have taken the mean of these two values. This value of s_{11} , together with the direct values of s_{12} and s_{13} , should satisfy equation 1, but does not exactly. I have adjusted the values of s_{12} and s_{13} in equations 3 and 5 by equal percentage amounts to satisfy 1. Equation 2 now gives a value for s_{33} for which there is no check, but which must be fairly good, since it involves the sum of two quantities. Equation 7 gives a single value for s_{44} , which is also fairly good, the measurements being easy and the difference involved being that of two quantities one twice the other. Equation 8 now gives a single value without check for s_{14} ; this value has much greater error than any of the others, since it was obtained from the difference of two quantities nearly equal ($20.3 - 17.1$). The final values for the constants obtained in this way are, in Abs. C. G. S. units:

$$\begin{aligned}s_{11} &= 17.7 \times 10^{-13}, \\s_{12} &= -3.8 \times 10^{-13}, \\s_{13} &= -8.5 \times 10^{-13}, \\s_{33} &= 33.8 \times 10^{-13}, \\s_{44} &= 41.0 \times 10^{-13}, \\s_{14} &= -8.0 \times 10^{-13}.\end{aligned}$$

The sign of s_{14} is the opposite of that found for bismuth. There does not seem to be any normal sign for this constant, but among the minerals examples of both signs have been found by Voigt.

Finally we have the linear compressibility as a function of pressure. The measurements were made in the regular way with the lever apparatus for short specimens, and the consistency of the results was that usual for this kind of measurement. The results are as follows: Parallel to trigonal axis

$$\begin{aligned}-\frac{\Delta l}{l_0} &= 16.48 \times 10^{-7}p - 20.5 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 16.37 \times 10^{-7}p - 18.0 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.}\end{aligned}$$

Perpendicular to trigonal axis

$$\begin{aligned}-\frac{\Delta l}{l_0} &= 5.256 \times 10^{-7}p - 4.56 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 5.091 \times 10^{-7}p - 3.04 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.}\end{aligned}$$

This gives for the cubic compressibility:

$$\begin{aligned}-\frac{\Delta V}{V_0} &= 26.99 \times 10^{-7}p - 31.6 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 26.55 \times 10^{-7}p - 25.3 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.}\end{aligned}$$

The unit of pressure is here the kg/cm².

The decrease of compressibility with rising temperature, both in the first and the second degree terms, is an unusual feature of the behavior of antimony.

Tellurium. The material used in all the final measurements was obtained from the Raritan Copper Works, who were so kind as to especially refine it for me in order to "completely" remove the 1% of selenium which is the principal impurity of the ordinary commercial material. Professor Saunders was kind enough to make a spectroscopic examination, and could find no selenium, but the spectroscopic test is known not to be sensitive. He did find some Ag and Cu, but no Fe, and considers it on the whole very pure.

Tellurium shows the same difficulty as bismuth in growing single crystal grains, but in an enhanced degree, in that the casting is very likely to consist of a number of grains all oriented very much alike. Toward the end of this work I found that this could be avoided by rapid cooling, and I obtained several rods 6 mm. in diameter which were single grains. The preferred direction of growth is exactly the same as with the other metals, that is, with the plane of easiest cleavage parallel to the axis of the casting. The analogy with the other metals ceases here, however, for in tellurium the cleavage on the

basal plane, perpendicular to the axis of three-fold symmetry, is not at all well developed, but there are three planes of principal cleavage, inclined at 60° to each other and intersecting along parallel lines parallel to the axis of three-fold symmetry. The preferred direction of growth is with all three planes parallel to the axis of the casting, that is, with the three-fold axis parallel to the length, whereas with the other metals the axis of rotational symmetry is usually perpendicular to the length. Inclination of the cleavage planes to the length is facilitated by rapid crystallization. The limiting velocity which I was able to use for the 6 mm. rods, with a wall thickness of the glass mold of about 1 mm. was about 1 cm. per minute, lowering into oil. More rapid cooling produces crystallization in quite a different way, numerous nuclei starting at the walls, and growth proceeding radially toward the center, so that a microscopically crystalline aggregate is obtained, with the axes of all the grains on the radii of the cylinder. In fact one casting of this character was obtained with the 1cm. rate.

I found that the practice sometimes adopted of melting tellurium in an iron receptacle is fatal to purity, the alloying with iron, particularly at the higher temperatures, being comparatively rapid.

There is one difficulty unique to tellurium among the metals I have tried. The thermal expansion along the axis is abnormal in being of the negative sign, so that when the mold is cooled the metal expands greatly relatively to the glass along the length, and sometimes pulls the glass apart. This is a disadvantage, because internal strains are thereby produced which in this very brittle metal may produce partial separation of the cleavage planes. When I have occasion to try this metal again, I shall make the mold of as thin glass as possible.

Thermal Expansion. This was measured in the regular way with the regular apparatus, using two specimens whose linear compressibility was also measured. One of these was parallel to the trigonal axis, and was a single piece 2.7 cm. long. The second was perpendicular to the trigonal axis (one set of cleavage planes perpendicular to the length) and was also one piece, but was only 1.1 cm. long. The thermal expansion for a small range in the neighborhood of room temperature was:

$$\alpha_1 = + 27.2 \times 10^{-6},$$

$$\alpha_{11} = - 1.6 \times 10^{-6}.$$

The expansion is positive, as is normal, across the cleavage planes, that is, the cleavage planes tend to separate at the higher temperatures, presumably resulting in easier cleavage.

The volume expansion given by the linear expansions above is 52.8×10^{-6} , which is normal in magnitude for a metal.

Electrical Resistance. The resistance measurements on tellurium were often inconsistent, doubtless because of the formation of fissures along the cleavage planes by the internal stresses incident to cooling. I have made no measurements of the temperature or pressure coefficients, but have made a careful examination of the specific resistance. Even the best castings were not uniformly good, but have bad places in them, so that it is necessary to make a very careful examination. Resistance was measured in the regular way with the potentiometer, but the potential terminals were only 1 cm. apart, and these were moved along the specimen by small amounts (a few mm. at a time) and a resistance exploration made of the whole rod. It was usually possible to find lengths of several cm. over which the resistance remained constant and a minimum. The specific resistance was calculated from the resistance of these localities. The results are shown in Figure 9, together with the curve of the most probable resistance.

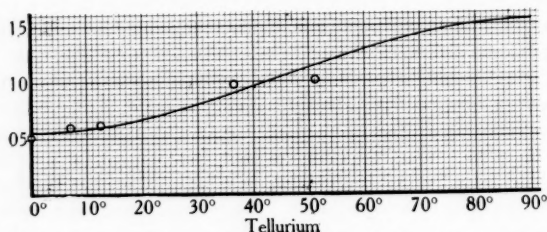


FIGURE 9. The specific resistance of tellurium at 20° C. as a function of the angle between the trigonal axis and the direction of flow.

I attempted to get the resistance perpendicular to the cleavage planes by the device of measuring the longitudinal resistance of one of the radially developed castings described above, but the values so found were impossibly high and had to be discarded. The explanation is without doubt to be found in fissures developed in the radial casting during cooling because of unequal thermal contractions in different directions.

The figure gives for the specific resistance at room temperature parallel to the trigonal axis 0.056 and perpendicular 0.154. The resistance is thus greatest across the cleavage planes, which is normal. The average resistance for the haphazard aggregate may be found to be 0.0973 ohms per cm. cube at 20° C.

This value for the resistance is much higher (30 times) than that which I have previously found for a specimen whose resistance under pressure I have measured,⁴ and is doubtless to be explained by the much greater purity of the present specimen. So far as I know, this is the only example of the resistance being increased by increasing purity. It is perhaps not so surprising when one considers that tellurium is non-metallic in character in many respects, and that its specific resistance is of the order of 10000 times higher than that of its metallic impurities.

Comparisons of the value of the specific resistance found above with other values are of uncertain significance, because the higher resistance which we have seen to go with higher purity may equally well be explained by the presence of the fissures which are almost unavoidably formed in the crystalline aggregate. However it is worth while to record that Beckman¹⁷ has found for the specific resistance values ranging from 0.05 to 0.62, and Matthiesen¹⁸ gives the values 0.2. These are of the order of that given above.

Elastic Constants. Tellurium has six elastic constants, as do also bismuth and antimony, but I was not able to obtain a specimen of suitable orientation, and therefore have no value for the cross constant s_{14} . The other constants were obtained as follows. In the first place there are measurements of the linear compressibility in two directions, equations 1 and 2. Then there are direct determinations of s_{33} and s_{13} from the longitudinal compression under one-sided compression of an unmachined casting with length parallel to the trigonal axis, equations 3 and 4, a direct value of s_{12} from the lateral expansion under one-sided compression of one of the compressibility pieces, equation 5, and another direct value for s_{33} from the extension under tension of an unmachined rod, equation 6. For the shearing constant s_{44} there are torsion measurements on two rods with axis parallel to the length, giving directly (without the use of the other elastic constants) values of s_{44} , equations 7 and 8. The equations for the constants follow.

$$(1) \quad s_{11} + s_{12} + s_{13} = 28.0 \times 10^{-13},$$

$$(2) \quad 2s_{13} + s_{33} = -4.2 \times 10^{-12},$$

$$(3) \quad s_{33} = 24.4 \times 10^{-13},$$

$$(4) \quad s_{13} = -12.2 \times 10^{-13},$$

$$(5) \quad s_{12} = -6.85 \times 10^{-13},$$

$$(6) \quad s_{33} = 23.7 \times 10^{-13},$$

$$(7) \quad s_{44} = 56.8 \times 10^{-13},$$

$$(8) \quad s_{44} = 59.4 \times 10^{-13}.$$

In selecting the compromise values to fit these equations, I assumed as always that the linear compressibility measurements are correct, although there is in this case no check by means of the cubic compressibility, which apparently has not been measured previously. For the two constants s_{33} and s_{13} , there are four equations to be satisfied. I made 2 exact, doing as little violence to the others as possible. The adjustment necessary was not serious, so that these constants must be regarded as fairly well established. For the two constants s_{11} and s_{12} we have only two equations 1 and 4. and there is no check, but nevertheless the results must be fairly good, because s_{12} is the result of a direct measurement, and s_{11} is the sum of positive terms. Finally for s_{44} we have the mean of equations 7 and 8, differing from each other by 4.5%. The final values for the constants in Abs. C. G. S. units are:

$$s_{11} = 48.7 \times 10^{-13},$$

$$s_{12} = -6.9 \times 10^{-13},$$

$$s_{13} = -13.8 \times 10^{-13},$$

$$s_{33} = 23.4 \times 10^{-13},$$

$$s_{44} = 58.1 \times 10^{-13},$$

$$s_{14} = \text{—————}.$$

For the linear compressibilities as a function of pressure we have measurements in the regular way and with the usual accuracy on specimens already described. The results in kg/cm² units for pressure are:

Perpendicular to trigonal axis,

$$\begin{aligned} -\frac{\Delta l}{l} &= 27.48 \times 10^{-7}p - 52.7 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 27.77 \times 10^{-7}p - 53.6 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

Parallel to trigonal axis,

$$\begin{aligned} +\frac{\Delta l}{l} &= 4.137 \times 10^{-7}p - 9.6 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 5.132 \times 10^{-7}p - 13.2 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

Notice the astonishing fact that the compressibility along the trigonal axis is negative, that is, when the crystal is subjected to a hydrostatic pressure all over it elongates along the trigonal axis. This result I have already found for a casting made by slow cooling, but the precise numerical value was not obtained. Of course the cubic compressibility is of the normal sign, as may be seen from the very much larger compressibility of the normal sign in the perpendicular direction, and as it must be because of conditions of stability.

The cubic compressibility to be obtained from the above linear compressibilities is:

$$\begin{aligned} -\frac{\Delta V}{V_0} &= 50.82 \times 10^{-7}p - 101.1 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 50.41 \times 10^{-7}p - 85.6 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

The cubic compressibility thus decreases at high temperatures. The compressibility is about twice that of antimony. If one tries to connect this value of the compressibility with the periodic properties of the elements, as Professor Richards³ has done with his curves of compressibility, it will be found that when plotted as a function of atomic weight in the usual way it falls entirely off the curve, coming after iodine in weight and being much less compressible. But when plotted against atomic number, the relative positions of iodine and tellurium are reversed, and the compressibility now comes between that of antimony and iodine, as does also the atomic number.

Tin. The material used was sometimes melting point tin from the Bureau of Standards (the analysis has been published in connection with my previous work on compressibility and resistance, the total impurity being about 0.012%), and sometimes Kahlbaum's purest tin. There appeared no difference between tin from the two sources, the electrical resistance being the same, and they have been used indiscriminately in obtaining the final results.

Tin is among the more difficult, of the metals tried here, to produce in single grains, there often being a reversion from one grain to another so that the first part of the rod is one grain and the rest another of entirely different orientation. The slowest rates of crystallization

produced the best results. It is also necessary to pay scrupulous attention to removing all specks of dirt and all occluded air. There seems no such unique preference as to manner of growth which some of the other metals show, but the axis of four-fold symmetry prefers to be either parallel or perpendicular to the length of the casting; I obtained no castings with angles between 20° and 74° .

More trouble was experienced in locating the axes of the crystal than with most other metals. Before the necessity of scrupulous freedom from all film of oxide on the surface was recognized I obtained several rods which appeared at first sight to be single crystals, but later were found to be multiple. This is probably connected in some way with the polymorphic transition which tin experiences on cooling below 160° . I found that the existence of several grains could be brought out by etching with dilute HCl with a few per cent chromic acid. Doubtless the reflection pattern shown before etching is that appropriate to the high temperature modification, whereas of course, the etching brings out the actual present structure of the crystal. With removal of all oxide and the obtaining of perfectly clean castings, this difficulty disappeared, however. It would seem that the surfaces of the microscopic pits undergo change also on passing through the transition point if there is no surface coating to hinder them.

The reflection pattern of the ordinary modification shows perfectly the tetragonal symmetry of tin, and affords a perfect method of identifying the crystallographic axes, but I nevertheless experienced considerable trouble at first because it appears that tin does not develop the basal plane perpendicular to the tetragonal axis as one of the surfaces of the reflection pattern, as do most of the other metals. The pattern which is usually developed is composed of the $\{111\}$ and the $\{110\}$ planes. Of course all these planes do not usually appear, because of unfavorable situation for reflection. I found that the construction of a card board model of the complete reflection pattern was of considerable assistance.

Examination of the reflection pattern may well be supplemented by examination of the mechanical flow pattern, particularly that obtained by compressing a short cylinder between polished steel platens. For some orientations slip takes place discontinuously on the basal planes with a slight click, leaving a beautiful tracery of parallel slip lines on the flat faces. In other orientations the circular section of the cylinder changes into a perfect ellipse, the generating lines of the cylinder remaining straight. I tried to develop the

possibility of cleavage in tin by violent deformation at liquid air temperatures, but the plasticity persists and no cleavage appears. A similar attempt with cadmium was also without success.

After the special details of growth and identification had been worked out, I was successful in obtaining castings of all sizes from 2 mm. to 2.2 cm. in diameter.

Thermal Expansion. The determinations were made in the regular way on the same specimens as those used for the linear compressibility. These were machined from a larger casting. The specimen perpendicular to the tetragonal axis was a single piece 2.76 cm. long; the parallel specimen was in two pieces of total length 2.44 cm.

The results for a small range of temperature in the neighborhood of room temperature are:

$$\alpha_1 = 15.45 \times 10^{-6},$$

$$\alpha_{11} = 30.50 \times 10^{-6}.$$

The expansion is nearly twice as great along the axis as at right angles; this is the normal direction of difference.

The average thermal expansion for a haphazard aggregate given by the above is 20.4×10^{-6} . This may be compared with 22.3 at 40° C. by Fizeau, and 23.0, mean between 0° and 100°, by Matthiesen. The difference is in the direction and of approximately the magnitude to be accounted for by the difference of temperatures.

Electrical Resistance. The specific resistance at room temperature was measured by all three methods described in the introduction. The crystal structure of tin seems less likely to be upset by machining than that of some of the other metals (the deformability not being as extreme as it is for cadmium and there being no cleavage) and much more consistent results were obtained with the methods requiring machining than were obtained with the other metals.

The collected results for the specific resistance at 20° C. are shown in Figure 10. The circles are the results for the natural unmachined rods, the crosses for the machined 3 mm. rod between copper terminals, and the crosses within the circles the data obtained by the four point method. The results with the unmachined rods are to be given the greatest weight, and they all seem to lie on the theoretical curve with an error considerably less than 1%. The specific resistances to be deduced from the figure are 9.90×10^{-6} perpendicular to the tetragonal axis, and 14.30×10^{-6} parallel to the axis.

The average specific resistance for a collection of haphazard crystals calculated from the above is 11.06×10^{-6} . This is materially less than the value 11.5 at the same temperature given in the Bureau of Standards circular. The difference is in the direction to be accounted for by greater purity of my sample.

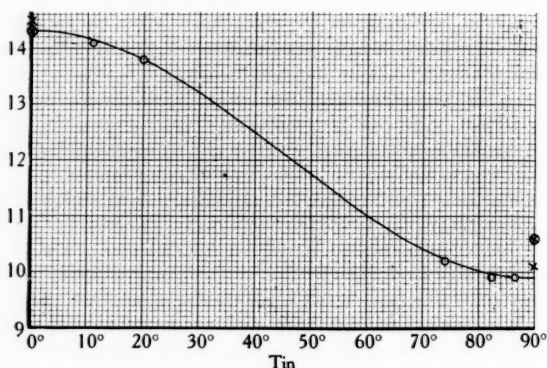


FIGURE 10. The specific resistance of tin at 20° C. as a function of the angle between the tetragonal axis and the direction of flow.

The variation of resistance with temperature at atmospheric pressure was measured for the two unmachined rods inclined at 11° and 74° with the length. The 11° rod was measured up and down the temperature range with a very small permanent change of resistance; the 74° rod was only measured up, and at the two extremes, but the permanent change of resistance after a pressure change of 12000 kg. was inappreciable, so that there is every reason to anticipate no trouble with the temperature effects.

Temperature	11° rod Resistance	74° rod Resistance
0°	1.000	1.000
25	1.107	
50	1.217	
75	1.330	
100	1.446	1.464

The temperature coefficient thus appears greatest perpendicular to the axis, which is the direction in which the resistance is least, so that the differences of resistance with direction become less accen-

tuated at higher temperatures. The temperature coefficient of specific resistance in these two directions may be found to be 0.00446 at 11° (correction inappreciable), and 0.00467 at 74° . Now to find the temperature coefficients of specific resistance along and at right angles to the axis we have two simultaneous equations in terms of the values for the 11° and the 74° directions. Solving the equations, we find for the average temperature coefficient of specific resistance between 0° and 100° C.:

Parallel to the tetragonal axis 0.00447,

Perpendicular to the tetragonal axis 0.00469.

I have previously found for the mean coefficient of measured resistance of extruded wire of Kahlbaum's tin the value 0.00447, essentially the value above for the direction parallel to the axis.

The effect of pressures to 12000 kg. on the resistance at 0° and 95° C. was measured on the same 11° and 74° specimens discussed above. The usual method was used with the usual accuracy, the deviations from a smooth curve of the average reading being of the order of a few tenths of a per cent. The resistance decreases under pressure, as is normal, and the rate of decrease itself becomes less at the higher pressures. At 0° C. the relation between pressure and resistance was representable by a second degree equation in the pressure within the limits of error, but at 95° the relation could not be given so simply. I have represented the results at this temperature in the way previously adopted, namely giving the average pressure coefficient between 0 and 12000 kg., and tabulating in addition as a function of pressure the correction term which must be added to the decrease of resistance calculated by a linear relation with the mean coefficient. The results follow.

Tetragonal axis 11° to length:

$$0^\circ \text{ C.} \quad -\frac{\Delta R}{R_0} = 1.043 \times 10^{-6}p - 9.35 \times 10^{-11}p^2, \quad (p \text{ in kg./cm}^2).$$

$$95^\circ \quad \text{Average coefficient to 12000} - 9.576 \times 10^{-6}.$$

The deviations from linearity are given in Table III.

Tetragonal axis 74° to length:

$$0^\circ \text{ C.} \quad -\frac{\Delta R}{R_0} = 9.696 \times 10^{-6}p - 9.70 \times 10^{-11}p^2,$$

$$95^\circ \quad \text{Average coefficient to 12000} - 8.453 \times 10^{-6}.$$

The deviations from linearity are given in Table III.

TABLE III

Pressure kg/cm ²	Deviations from Linearity	
	11° rod	74° rod
0	.00000	.00000
1000	.00146	.00118
2000	257	202
3000	335	268
4000	398	309
5000	420	333
6000	409	325
7000	370	295
8000	325	258
9000	263	204
10000	191	148
11000	107	81
12000	.00000	.00000

This method of representing the results will be made clearer by an example. Thus suppose we wish to find the change of resistance at 95° C. of the 74° rod under 8000 kg/cm². The decrease calculated by the linear relation, using the average coefficient above, is $8000 \times 8.453 \times 10^{-6}$, which is equal to 0.06762. To this is to be added the deviation from linearity given in the table for 8000 kg, or 0.00258, making for the decrease 0.07020. That is, the resistance of this rod at 95° C. under 8000 kg. is 0.92980 of the resistance at atmospheric pressure at 95° C.

The above results show that the decrease of resistance under pressure is most rapid in the direction of the axis, that is, the direction in which the specific resistance is the greatest. The differences of resistance with direction in the crystal thus become less accentuated at high pressures. This is also the effect of increasing the temperature; it is more usual that the effect of an increasing pressure is similar to that of a decreasing temperature. The pressure coefficients of resistance in different directions vary much less than the specific resistances in those directions, so that the equalizing of resistance by pressure is a very slow process.

With the values of the elastic constants to be given presently we may calculate that the initial pressure coefficients of resistance at 0° C. are:

$$\begin{aligned} \text{Tetragonal axis } 11^\circ \text{ to length} &= 1.095 \times 10^{-5}, \\ \text{" " } 74^\circ \text{ " "} &= 1.035 \times 10^{-5}. \end{aligned}$$

The difference of measured coefficient with direction is hence nearly the same as the difference of specific coefficient with direction.

The formulas of the introduction now enable us to find the pressure coefficient of specific resistance perpendicular and parallel to the axis. We find at 0° C.:

Initial pressure coefficient of specific resistance
parallel to the axis -10.96×10^{-6} .

Initial pressure coefficient of specific resistance
perpendicular to the axis -10.28×10^{-6} .

Elastic Constants. Tin being tetragonal, has six elastic constants. It differs from the metals hitherto measured in that there are two independent shearing constants, so that it is necessary to somewhat modify the procedure. It is fortunate that castings could be obtained with the axis nearly parallel and nearly perpendicular to the length. The following equations were obtained for the elastic constants.

$$(1) \quad 2s_{13} + s_{33} = 6.83 \times 10^{-13},$$

$$(2) \quad s_{11} + s_{12} + s_{13} = 6.13 \times 10^{-13},$$

$$(3) \quad s_{11} = 17.3 \times 10^{-13},$$

$$(4) \quad .9876s_{11} + .0037(2s_{13} + s_{44}) + .0012(2s_{12} + s_{66}) = 20.3 \times 10^{-13},$$

$$(5) \quad .9876s_{11} + .0037(2s_{13} + s_{44}) + .0012(2s_{12} + s_{66}) = 15.2 \times 10^{-13},$$

$$(6) \quad .9540s_{11} + .0168(2s_{13} + s_{44}) + .0061(2s_{12} + s_{66}) = 22.2 \times 10^{-13},$$

$$(7) \quad .0012s_{11} + .9283s_{33} + .0351(2s_{13} + s_{44}) = 20.1 \times 10^{-13},$$

$$(8) \quad .9662(s_{11} - s_{12}) + .4834s_{44} \\ + .0167\{2(s_{11} + s_{33} - 2s_{13}) \\ + \frac{1}{2}(s_{66} - s_{44})\} + .4709\{s_{66} - 2(s_{11} - s_{12})\} = 83.7 \times 10^{-13},$$

$$(9) \quad .9926(s_{11} - s_{12}) + .4963s_{44} \\ + .0037\{2(s_{11} + s_{33} - 2s_{13}) \\ + \frac{1}{2}(s_{66} - s_{44})\} + .4926\{s_{66} - 2(s_{11} - s_{12})\} = 106. \times 10^{-13},$$

$$(10) \quad .0013(s_{11} - s_{12}) + .9290s_{44} \\ + .0352\{2s_{11} + 2s_{33} - 4s_{13} - \frac{1}{2}s_{44} + \frac{1}{2}s_{66}\} = 56.8 \times 10^{-13},$$

The equations are more complicated than for the previous substances. The complication arises from the fact that when deformations are measured of rods inclined to the axis, it is necessary to know the

position of the three crystallographic axes, instead of merely the axis of rotational symmetry, which sufficed in all previous cases except for the constant s_{14} of the trigonal system. The equations were obtained as follows. 1 and 2 are given by linear compressibility measurements of the samples already described under thermal expansion. These equations are taken as correct in the calculations. A check is afforded by the cubic compressibility calculated from them, which is 19.09×10^{-13} , against 18.7 by Adams, Williamson, and Johnston, and 19 by Richards. Equation 3 comes from the longitudinal compression under one-sided compression of one of the compressibility samples. 4 comes from the longitudinal compression under one-sided compression of an unmachined casting with axis at 86.5° to the length, 5 from the extension under tension of the same rod as used in 4, and 6 from the extension under tension of an unmachined rod with axis at 82.5° to the length. 7 is from the extension under tension of an untouched rod with axis at 11° to the length. 8 and 9 are from torsion measurements of the rods of equations 4 and 6, and 10 from torsion of the rod of equation 7.

It will be noticed that some of the equations contain predominantly only one of the constants, as 4, 5, and 6 contain predominantly s_{11} . Hence, in these, very rough values for the other constants will suffice, which may be obtained by a solution of a sufficient number of the other equations. In solving the equations I first obtained the value of s_{11} from 3, 4, 5, and 6 (using the approximate values of the other constants as already explained). The values so found were 17.3×10^{-13} , 20.2, 21.4, and 15.2 respectively. As the best value of s_{11} I took the average, 18.5×10^{-13} . Equation 7 gives a value of s_{33} , 11.8×10^{-13} . These values now substituted into 1 and 2 give the values accepted as final for s_{12} and s_{13} . This completes the list of rectangular constants. For the shearing constants there are equations 8, 9, and 10. 8 and 9 are of approximately the same form, and I took the average of these, averaging the coefficients straight through. The average differs from the extremes by something of the order of 15%, so that the accuracy is not high. Equation 10 differs in form markedly from the average of 8 and 9. These two equations were now solved simultaneously for s_{14} and s_{66} .

Of the constants obtained by the procedure above it will be seen that there are no checks on s_{33} , s_{12} , and s_{13} . The first of these should be fairly good, since it is given essentially by direct measurement. The two others are less certain. The check on the shearing constants, which consists of three equations for two quantities, is not as close

as desirable, but the essential result cannot be in doubt that s_{66} is much larger than s_{44} .

The final results are:

$$s_{11} = 18.5 \times 10^{-13},$$

$$s_{12} = -9.9 \times 10^{-13},$$

$$s_{13} = -2.5 \times 10^{-13},$$

$$s_{33} = 11.8 \times 10^{-13},$$

$$s_{44} = 57.0 \times 10^{-13},$$

$$s_{66} = 135. \times 10^{-13}.$$

The second shearing constant s_{66} differs greatly from the value which it would have in the hexagonal, trigonal, or cubic systems. In these systems we have the relation $s_{66} = 2(s_{11} - s_{12})$. Substituting the values above for tin, the right hand side of the equation becomes 56.8 against 135 experimental, or less than half.

We have finally the linear compressibility as a function of pressure to 12000 kg. The measurements were made in the small lever apparatus, using the specimens described under thermal expansion. The data were of the usual regularity, and gave the following results, pressure in kg/cm².

Length perpendicular to tetragonal axis

$$\begin{aligned} -\frac{\Delta l}{l_0} &= 6.022 \times 10^{-7}p - 4.20 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 6.144 \times 10^{-7}p - 4.26 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

Length parallel to tetragonal axis

$$\begin{aligned} -\frac{\Delta l}{l_0} &= 6.719 \times 10^{-7}p - 4.07 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 6.956 \times 10^{-7}p - 3.91 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

The linear compressibility is thus greatest across the basal plane, which is normal. The difference of compressibility in different directions is, however, much less than normal.

The change of volume as a function of pressure is:

$$\begin{aligned} -\frac{\Delta V}{V_0} &= 18.76 \times 10^{-7}p - 13.6 \times 10^{-12}p^2, & \text{at } 30^\circ \text{ C.} \\ &= 19.24 \times 10^{-7}p - 13.7 \times 10^{-12}p^2, & \text{at } 75^\circ \text{ C.} \end{aligned}$$

MAGNETIC PROPERTIES.

A very rough examination was made for differences of magnetic permeability in different directions. The single crystal, in the form of a cylinder about 1.25 cm. in diameter and 2.8 cm. long, was suspended by a comparatively heavy strand of silk with its axis vertical between the conical poles of an electro-magnet giving something of the order of 15000 Gauss. The principal axis of the crystal was perpendicular to the vertical axis of the cylinder. Any tendency to orientation in a definite direction was observed. Results were found only with bismuth and antimony, and here the effects were large, there being a very strong directive action. Bismuth sets itself with the trigonal axis parallel to the lines of force. That is, the magnetic permeability is algebraically greatest along the trigonal axis in bismuth. This observation was made a long time ago, perhaps first by Tyndall. But antimony acts oppositely, setting itself with the *cleavage plane* parallel to the lines of force. The action is, if anything, stronger than in bismuth. So far as I know, this observation is new.

No effect was found with the other metals. This may have been partially masked by the very sluggish action in the magnetic field due to eddy current damping. An interesting effect was found with tin. There is no effect on making the magnetic field, but if the field is destroyed when the tetragonal axis is inclined to the lines of force, there is a rotational kick, in such a direction as to align the tetragonal axis and the magnetic lines. The kick vanishes if the axis originally lies along the lines of force. The effect is evidently due to a reaction between the eddy currents induced in the tin and the magnetic field, the eddy currents not being in the plane perpendicular to the lines of force when the axis is not parallel because of the inequality of specific resistance in different directions. The effect was not found with the other metals; the difference of resistance of tin in different directions is greater than of the other metals.

SUMMARY AND GENERAL SURVEY OF RESULTS.

In Table IV are collected some of the principal results, namely the linear compressibilities, the two elastic constants s_{11} and s_{33} which give the extensions under simple tensions in the principal directions, the thermal expansion, the specific resistance, the temperature coefficient of specific resistance, and the initial pressure coefficient of specific resistance. In the detailed presentation, all the elastic

TABLE IV.
SUMMARY OF RESULTS ON NON-CUBIC METALS.

Metal	Initial linear Compressibility at 30° Pressure unit, 1 kg/cm ²	Elastic Constants Abs. C. G. S. s_{11} 1 s_{33} 11	Linear Thermal Expansion at 20° C.	Specific Resistance at 20° C.	Average Temperature Coefficient of Specific Resistance 0°-100° C.	Initial Pressure Coefficient of Specific Resistance at 0° C. Pressure in kg.
Zn 11 1	12.98×10^{-7} 1.95	26.38×10^{-13} 8.23	57.4×10^{-6} 12.6	6.13×10^{-6} 5.91	.00419 418	-10.87×10^{-6} -6.55
Cd 11 1	18.3 2.1	36.9 12.9	52.5* 20.2*	8.30 6.80	428(?)	-13.1 -8.7
Bi 11 1	15.92 6.62	28.7 26.9	13.96 10.36	138. 109.	445	+24.5 +7.5
Sb 11 1	16.48 5.26	33.8 17.7	15.56 7.96	35.6 42.6	595 511	+17.2 +1.05
Te 11 1	-4.14 27.48	23.4 48.7	-1.6 27.2	56000. 154000.		
Sn 11 1	6.72 6.02	11.8 18.5	30.50 15.45	14.3 9.9	447 469	-10.96 -10.28

* From Grüneisen and Goens.

constants are given, and the effect of pressures to 12000 kg/cm² on the other properties. In addition to the results on non-cubic metals shown in the Table, the elastic constants and compressibility of a single tungsten crystal have been determined.

It is evident that the cleavage plane, or plane of easiest slip in case the crystal does not cleave (this plane is also the basal plane perpendicular to the axis of rotational symmetry for all the metals except tellurium), corresponds to some fundamental fact in the crystal structure which is reflected in the other properties. The atoms are connected more loosely across the cleavage plane, so that external forces produce greater effects in this direction than in others. The linear compressibility is always greatest across the cleavage plane, and in fact in the case of tellurium the linear compressibility is negative in the cleavage plane. The extensibility under tension (effective Young's modulus) is also greatest across the cleavage plane, with the exception of tin, in which the reversal is rather surprisingly large in magnitude. The thermal expansion is also greatest across the cleavage plane, and in the case of tellurium the expansion in the plane is actually negative. The specific resistance is also greatest for current flow across the cleavage plane, with the exception of antimony, which, however, constitutes only a temporary exception, as it becomes normal under high pressure. The temperature coefficients of resistance do not seem to show large variations with direction, with the exception of antimony, which again may be regarded as a temporary anomaly disappearing at high pressures. The effect of pressure on specific resistance is also greatest across the cleavage plane, whether that effect is an increase or a decrease of resistance (tellurium not measured).

A detailed examination does not show any striking quantitative uniformities, but in general the statement is justified that the various electrical properties show much less variation with direction than do the elastic properties or the thermal expansion. This is in general agreement with what we might expect, the elastic constants being intimately associated with a property of the atoms somewhat like that of a rigid boundary, which prevents them from telescoping into each other when pushed together, whereas the rigid boundaries do not so effectively exist for that migration of the electrons which constitutes the electrical current.

The most interesting special results are probably the negative expansion and compressibility of tellurium along the axis, the maximum of resistance and the reversal of the axial ratio at high pressures

of antimony, and the two new high pressure modifications of cadmium.

We are not yet in a position to give a theoretical account of these results, so simple a thing as the shearing constant of rock salt being as yet unexplained. It is perhaps significant that the shearing constant of a crystal of tungsten has been found to be connected with the other two constants by nearly the same relation as in an isotropic body.

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REFERENCES.

- ¹ E. v. Gomperz, *ZS. f. Phys.* 8, 184-190, 1922.
- H. Mark, M. Polanyi, and E. Schmid, *ZS. f. Phys.* 12, 58-78, 1922.
- H. Mark and M. Polanyi, *ZS. f. Phys.* 18, 75-97, 1923.
- H. C. H. Carpenter and C. F. Elam, *Proc. Roy. Soc.* 100, 329-353, 1921.
- ² E. Grüneisen and E. Goens, *Phys. ZS.* 24, 506-510, 1923.
- ³ P. W. Bridgman, *Proc. Amer. Acad.* 58, 166-242, 1923.
- ⁴ P. W. Bridgman, *Proc. Amer. Acad.* 56, 61-154, 1921.
- ⁵ P. W. Bridgman, *Proc. Amer. Acad.* Paper to be published on the effect of tension on resistance longitudinally and transversely.
- ⁶ W. Voigt, *Lehrbuch der Krystallphysik*, Teubner, 1910, section 173 and ff.
- ⁷ Zay Jeffries, *Jour. Amer. Inst. of Metals*, 11, 300-324. *Trans. Amer. Inst. Mining Eng.* New York meeting, Feb. 1919.
- ⁸ T. W. Richards, *Carnegie Inst. Wash. Publication No.* 76, 1907.
- ⁹ L. H. Adams, E. D. Williamson and J. Johnston, *Jour. Amer. Chem. Soc.* 41, 1, 1919.
- ¹⁰ W. Jaeger and H. Diesselhorst, *Phys. Tech. Reichsanstalt, Wiss. Abh.* 3, 269-425, 1900.
- ¹¹ L. Holborn, *Ann. Phys.* 59, 145-169, 1919.
- ¹² Ernst Cohen, *Jour. Amer. Chem. Soc.* 40, 1149-1156, 1918. Other references are given in this paper.
- ¹³ P. W. Bridgman, *Proc. Amer. Acad.* 57, 41-66, 1921.
- ¹⁴ Ch. Matteucci, *C. R.* 40, 541, 913, 1855; 42, 1133, 1856.
- ¹⁵ G. Borelius and A. E. Lindh, *Ann. Phys.* 51, 606-620, 1916.
- ¹⁶ E. v. Everdingen, *Versl. Kon. Akad. Amst.* 1896-97, 494-502.
- ¹⁷ B. Beckman, *Ann. Phys.* 46, 931-940, 1915.
- ¹⁸ A. Matthiesen, *Pogg. Ann.* 103, 428-434, 1858.

